

A study of methyl halide fluxes in temperate and tropical ecosystems



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Abstract

CH₃Br and CH₃Cl (methyl halides) are the most abundant natural vectors of bromine and chlorine into the stratosphere and play an important role in stratospheric ozone destruction. The current knowledge of their respective natural sources is incomplete leading to large uncertainties in their global budgets. Beside the issue of quantification, characterisation of possible sources is needed to assist modelling of future environmental change impacts on these sources and hence the stratosphere. This study describes measurements conducted at two temperate salt marsh and three temperate forest sites in Scotland, and one tropical rainforest site in Malaysian Borneo to quantify and characterise natural methyl halide producing processes in these respective ecosystems.

Measurements were conducted with static enclosure techniques, and methyl halide fluxes were calculated from the concentration difference between blank/background and after-enclosure samples. Methyl halide concentrations were determined via oxygen-doped GC-ECD with a custom-built pre-concentration unit. External factors such as photosynthetically-active radiation (PAR), total solar radiation, air temperature, soil temperature, internal chamber temperature and soil moisture were recorded in parallel to the enclosures to determine possible dependencies.

Salt marsh studies were carried out at Heckie's Hole in East Lothian, and Hollands Farm in East Dumfriesshire for 2 years. The study subjects were salt marsh plants that were enclosed during daylight hours in transparent enclosures for 10 min each at 2–4 week intervals throughout the year. Parallel to this monitoring programme, systematic manipulation experiments and diurnal studies were carried out to learn more about the possible influence of potential drivers such as sunlight and temperature. Mean annual net fluxes (\pm standard deviation (sd)) were $300 \pm 44 \text{ ng m}^{-2} \text{ h}^{-1}$ for CH₃Br and $660 \pm 270 \text{ ng m}^{-2} \text{ h}^{-1}$ for CH₃Cl, with fluxes of both gases following a diurnal as well as an annual cycle, being lowest during winter nights and highest during summer days. A possible link between variations of daytime fluxes over the course of a year and changes in temperature was found. CH₃Cl and CH₃Br fluxes

were positively correlated to each other and average fluxes of CH₃Cl were linked to dry mass of certain species such as *Puccinellia maritima*, *Aster tripolium*, *Juncus gerardi* and *Plantago maritima* as found at the different measurement locations. No link between methyl halide fluxes and total halogen content or halogen concentration of the enclosed vegetation was found.

Work in temperate forests was carried out for over one year at Fir Links, a mixed beech/sycamore forest in East Lothian, and on one occasion each in Griffin Forest, a sitka spruce plantation in Perthshire, and finally the Hermitage of Braid, a mixed woodland park in Edinburgh. The study subject was leaf and needle litter which was enclosed in opaque 12 L containers for 10 min–24 h. During enclosure, internal chamber temperature was recorded, and leaf/needle litter water content was determined after enclosure. Combined average CH₃Br and CH₃Cl fluxes from temperate forest litter were $4.3 \times 10^{-3} \text{ ng g}^{-1} \text{ h}^{-1}$ and $0.91 \text{ ng g}^{-1} \text{ h}^{-1}$, respectively. Average fluxes measured from leaf and needle litter were comparable in magnitude and CH₃Br and CH₃Cl were positively correlated. However no correlation of methyl halide fluxes to either temperature or litter water content was observed.

Work at Danum Valley in Malaysian Borneo focused on flux measurements from both trees and leaf litter in a tropical dipterocarp forest. Fluxes from tropical trees were measured with transparent branch chambers at 20 min enclosure times whilst methyl halide fluxes from leaf litter were measured with opaque 12 L containers at 24 h enclosure times. Mean CH₃Br and CH₃Cl fluxes from branch enclosures were $0.53 \text{ ng g}^{-1} \text{ h}^{-1}$ and $27 \text{ ng g}^{-1} \text{ h}^{-1}$, respectively, and CH₃Br and CH₃Cl fluxes from tropical leaf litter were $1.4 \times 10^{-3} \text{ ng g}^{-1} \text{ h}^{-1}$ and $2.3 \text{ ng g}^{-1} \text{ h}^{-1}$ respectively. Again fluxes of CH₃Br and CH₃Cl were positively correlated but no direct environmental driver for flux variations was found. The magnitude of methyl halide fluxes was species specific with individuals of the genus *Shorea* generally producing large amounts of methyl halide. Tropical rainforests were confirmed to be potentially the largest single natural source of CH₃Cl.

Global estimates were derived from extrapolating measured fluxes from the respective global land cover areas. These estimates suggest that the ecosystems examined in this study could account for over 1/3 of global CH₃Cl production and up to 13 % of global CH₃Br production in nature. The ratio of CH₃Br to CH₃Cl emissions for these ecosystems is likely to be dependent on the abundance of bromine in the plant material with higher bromine content boosting CH₃Br production and suppressing CH₃Cl production. For this reason salt marshes are only a very minor source of CH₃Cl.

Declaration

I hereby declare that this thesis was composed by myself and that the work described within is my own, except where explicitly stated otherwise.

Emanuel Blei

July 2010

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Chapter 1

Introduction

During the 20th and 21st century atmospheric sciences have played a leading role in the endeavour of mankind to understand nature and in the promotion of scientific evidence as a basis for political decision making. A prime example was an article by Farman et al. in 1985. After they reported the appearance of a large seasonal Antarctic ozone (O_3) hole the international community took the unprecedented step to phase-out and ban the use of chlorofluorocarbons (CFCs), halons and congeners. Due to these efforts the concentrations of these gases and their effect on the stratosphere is expected to subside to pre-1980 levels within the next 50 years [Fahey, 2007]. Parallel to the recent decline in emissions of these man-made gases came the awareness that natural processes are also contributing to halogen-related O_3 loss in the stratosphere and today it is recognised that with declining influence of man-made halocarbons the effect of natural emissions will become more apparent.

1.1 Methyl halides in the atmosphere

The main vectors of natural bromine and chlorine transport to the stratosphere have been identified as CH_3Br and CH_3Cl . Both of these gases have anthropogenic and natural origins, but it is only CH_3Br for which anthropogenic sources are large enough to be of relevance [Montzka et al., 2002; Clerbaux et al., 2007]. These two gases together with CH_3I are called methyl halides. However CH_3I is not significant for stratospheric O_3 depletion [Ennis, 2007] and therefore not considered in this work. Thus the term ‘methyl halides’ used throughout the remaining text of this thesis exclusively refers to CH_3Br and CH_3Cl .

Previously, manufactured CH_3Br was used for the fumigation of crops, perishables, durables and structures as an effective pesticide against weeds, vertebrates and invertebrates. In 1992 ~25 % of global CH_3Br emissions were of anthropogenic origin with the rest being produced by natural processes [Montzka et al., 2002]. However, the ozone depletion potential (ODP) of

CH_3Br , a measure of a substance's ability to destroy stratospheric O_3 relative to an equal mass of CCl_3F , is relatively high ($\text{ODP} = 0.51$) and its use was therefore phased out from 1996/1997 in accordance with the Montreal Protocol. Since then its atmospheric concentration has decreased by 14 % to currently 7.9 parts per trillion (10^{-12}) by volume (pptV) [Clerbaux et al., 2007].

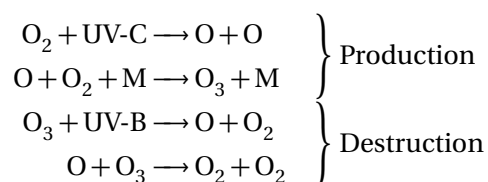
CH_3Cl is used industrially to produce silicone. This process does not release any appreciable amounts of CH_3Cl [OECD secretariat, 2003; Clerbaux et al., 2007]; nor do any other anthropogenic activities act as major sources of this gas. The ambient atmospheric CH_3Cl concentration is 550 ± 30 pptV and currently stable; its estimated ODP is 0.02 and it is not a controlled substance under the Montreal Protocol [Clerbaux et al., 2007].

1.2 Effect of CH_3Br and CH_3Cl on stratospheric O_3

This section provides a brief overview of the main chemistry relating to the impact of halogen-containing compounds on stratospheric O_3 .

1.2.1 The Chapman cycle

The Chapman cycle reactions (below) describe the photo-initiated conversion of molecular oxygen (O_2) to O_3 and back [Chapman, 1930]. The cycle occurs naturally in the stratosphere where, in the absence of other reactions, the concentration ratio of O_3 to O_2 would be solely determined by the relative rates of the two processes. The notation M in a chemical reaction represents any chemically inert collision partner (atom or molecule) which removes energy to stabilise an adduct product.

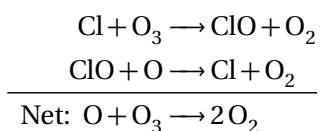


There are two important consequences of these reactions: (1) the absorption of UV-B ($\lambda = 315\text{--}280$ nm) and UV-C ($\lambda = 280\text{--}100$ nm) radiation filters out a large proportion of the short-wave radiation from the solar spectrum that causes cellular damage to living organisms on Earth's surface, greatly reducing the risk of cancer; (2) the heat released in the O_3 -formation reaction leads to the stable temperature inversion profile that exists within the stratosphere.

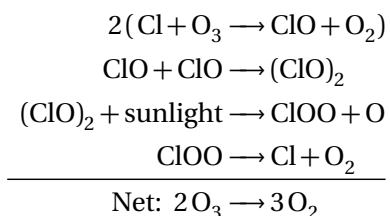
1.2.2 Additional catalytic O_3 depletion reactions

The O_3 to O_2 ratio found in the stratosphere is actually half the value expected if only the Chapman cycle were involved. Instead the direct reaction of atomic oxygen with O_3 only accounts for approximately one-quarter of total O_3 loss. The remaining three quarters are due to other reactions which involve catalytic conversion of O_3 back to O_2 . Catalytic conversion of O_3 to O_2 reduces the concentration of O_3 towards lower levels thereby leading to higher fluxes of UV-B radiation at Earth's surface. The catalysts of these reactions in the stratosphere are HO_x , NO_x and the halogen species ClO_x and BrO_x . Cl and Br are formed when halogen containing substances such as CFCs or methyl halides enter the stratosphere, where they are photolysed into free halogen radicals and organic residues.

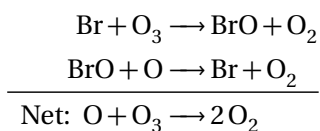
The chlorine and bromine radicals then catalyse the conversion of O_3 to O_2 according to the following reaction pathways [Fahey, 2007]:



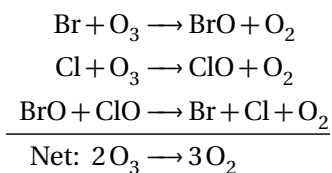
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as well as



A coupled cycle involving both chlorine and bromine is synergistic and enhances the catalytic efficiency of the separate chlorine and bromine cycles [Fahey, 2007; Yung et al., 1980]. Together they account for approximately 30 % of total natural stratospheric O_3 loss [Wayne, 2000].



Similar cycles exist for NO_x and HO_x , together with corresponding synergistic cycles involving two different species. In contrast to the combined $\text{ClO}_x + \text{BrO}_x$ -cycle, some of these cycles reduce the overall ODP of the individual species involved by either creating reservoir species or by creating null cycles both of which do not take part in O_3 depletion reactions [Yung et al., 1980; Wayne, 2000]. The overall reaction scheme is rather complicated and the different cycles are not equally important throughout the stratosphere but vary in significance with both latitude and altitude [Wayne, 2000]. It also must be emphasised that all these reactions occur naturally but can be enhanced by human activities.

Anthropogenic emissions of O_3 depleting substances account for a global decline in stratospheric O_3 of $\sim 4\%$ compared to 1980 levels. The effect of anthropogenic emissions on the Antarctic and Arctic ozone layers is more severe, leading to the infamous “ozone holes”. At both poles, but especially over Antarctica, stratospheric temperatures in winter fall below -78°C , which is the formation temperature of polar stratospheric clouds (PSCs). These clouds ‘trap’ NO_2 leading to the ‘denitrification’ of the stratosphere when they sink down towards the troposphere. Free NO_2 normally reacts with ClO and BrO to form the reservoir species ClONO_2 and BrONO_2 , respectively. However, once all NO_2 is trapped in PSCs the Cl and Br tied up in their respective reservoir species are released as reactive ClO and BrO . Furthermore other reservoir species, such as HCl are also converted into the reactive halogen monoxides via conversion on the cloud particles’ surfaces. During the same time the air above the Antarctic/Arctic is trapped within a polar vortex which prevents exchange of air masses with the rest of the atmosphere. However, even the catalytic reactions require either visible or UV-radiation to close the catalytic cycle and therefore the “ozone holes” normally occur during late winter or early spring when temperatures are still low and sunlight becomes available. The combined effect of the massive release of reactive halogen species, the occurrence of sunlight and the prevention of air exchange can lead to temporary O_3 losses of up to two thirds [Fahey, 2007]. Again the overall reaction scheme is rather complicated but for the purpose of this study the presented information is sufficient.

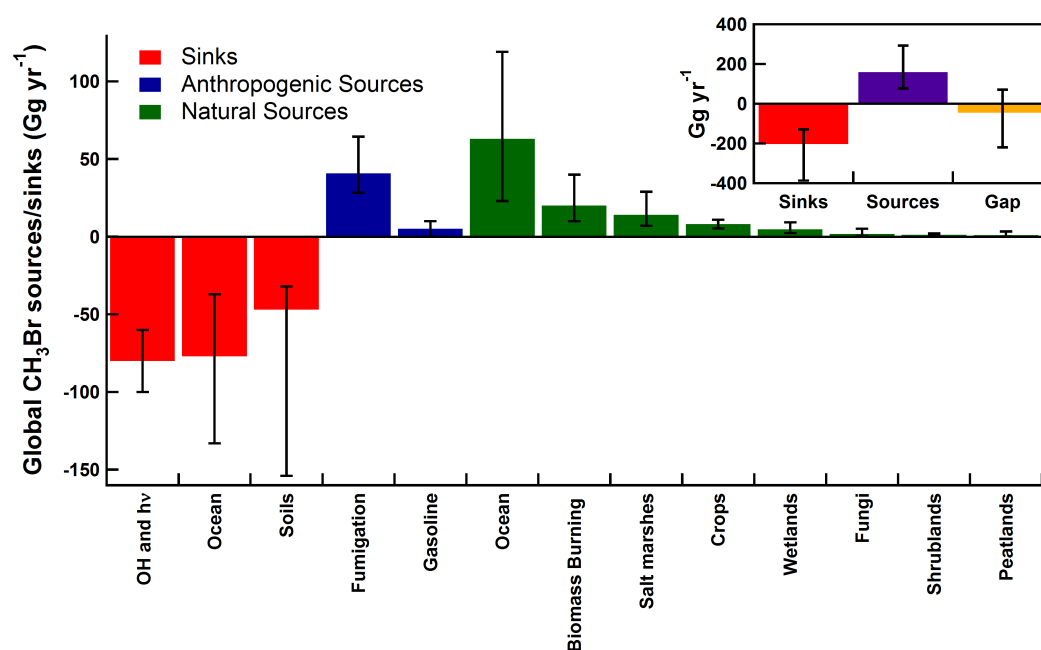
1.3 Why it is important to study methyl halide fluxes

It is estimated that currently CH_3Br and CH_3Cl account for $\sim 37\%$ and $\sim 16\%$ of bromine and chlorine related stratospheric O_3 loss [Fahey, 2007], respectively and combined they are responsible for $\sim 25\%$ of total halogen related O_3 loss [Butler, 2000]. Due to the fall in anthropogenic emissions of other halogen containing gases, their relative contribution to total halogen related O_3 loss is projected to rise to over 50% by 2100 [Fahey, 2007]. Methyl halides also form a link between the biosphere and atmosphere. Future environmental change, caused by anthropogenic greenhouse gas emissions and land use change, will influence methyl halides fluxes, and this will result in variations of stratospheric O_3 and will ultimately change global climate. It therefore is important to gain a deeper understanding of the role of methyl halides in nature in order to predict the effects of environmental change on the ozone layer. This, however, is proving difficult since the natural phenomena controlling production and consumption of methyl halides in nature are not sufficiently known.

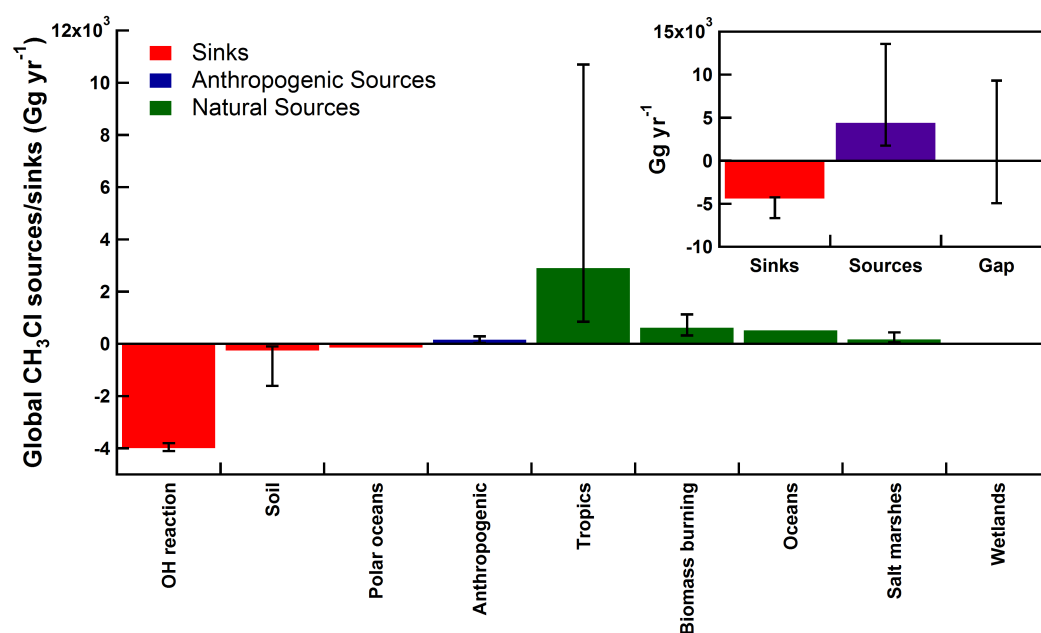
Figure 1.1 shows the latest estimated budgets of CH_3Br and CH_3Cl as derived from data in the World Meteorological Organisation (WMO) reports from 2002 and 2006. Both plots clearly show that the estimated methyl halide budgets have a high degree of uncertainty. A decline of global CH_3Br concentrations has been measured for several years indicating that current sinks are larger than corresponding sources. However, even when accounting for this gradual decline in CH_3Br concentrations, the better constrained sink terms for CH_3Br are considerably larger than known sources and, for both CH_3Br and CH_3Cl , the presented “best estimates” are often highly uncertain and tentative. This was highlighted to the wider science community in a series of articles led by Butler [2000] appearing in *Nature* in 2000. The article pointed out a shortfall of $\sim 50\text{--}75\%$ of known natural sources compared to the better constrained natural sinks of methyl halides. The other reports then featured new data of potential CH_3Br and CH_3Cl sources ranging from salt marshes [Rhew et al., 2000] to tropical vegetation [Yokouchi et al., 2000] and abiotic production mechanisms in soils [Keppler et al., 2000].

The reasons for the uncertainties in emissions inventories can be divided into three categories:

1. It is generally acknowledged that most of the missing sources of methyl halides must be terrestrial rather than oceanic, as data from cruises have shown that sea water is not sufficiently saturated in CH_3Cl to be a large enough source of this gas [Moore et al., 1996] whilst oceans are in fact a net sink of CH_3Br [Lobert et al., 1995; Butler, 2000]. Furthermore terrestrial ecosystems are very heterogeneous and therefore a large number of temporally and spatially resolved data are required to gain reliable global



(a) Best estimate values of global sources and sinks of CH_3Br as derived by Montzka et al. [2002] from references cited therein. The bar labelled 'Crops' represents emissions from rice and rapeseed plants. The inset chart displays best estimates of the total sum of sources, sinks and the gap between the two. Whiskers indicate the upper and lower range of values.



(b) Best estimate values of global sources and sinks of CH_3Cl as derived by Clerbaux et al. [2007] from references cited therein. The bar labelled 'Tropics' represents both tropical plants and leaf litter, 'Anthropogenic' sources include fossil fuel burning, waste incineration and other industrial emissions. The inset chart displays best estimates of the total sum of sources, sinks and the gap between the two. Whiskers indicate the upper and lower range of values, where they are available.

Figure 1.1: Current best estimate values of global annual sources and sinks of CH_3Br and CH_3Cl .

or even regional source estimates. However conducting field studies is expensive and labour intensive and therefore field data are often scarce or not representative enough for up-scaling.

2. Besides the need for a large number of long term measurements and, where possible, information of potential drivers, the global extent of an ecosystem, such as salt marshes, or a measure of certain quantities, such as the leaf litter density in g per m² for different forest types, are required. Although gathering such ancillary data can be partially conducted via remote sensing these pieces of information are still scarce.
3. The potential impact of ozone-depleting substances on the ozone layer expressed as ODP depends on both the number of bromine and chlorine atoms it contains as well as on its atmospheric lifetime. Atmospheric lifetime—defined as the time of decay from concentration x to concentration x/e —quantifies the time a molecule can travel in the atmosphere before it is destroyed by a number of possible processes. This means that highly brominated organic compounds might not have high ODPs since they are destroyed within minutes. The average time taken for a molecule released at mid-latitudes to travel to the tropical region, where the thermal uplift is strong enough to penetrate the tropopause and allow access to the stratosphere, ranges from weeks to months, and decreases the nearer a source is to the equator. The atmospheric lifetimes of CH₃Br and CH₃Cl are 0.7 yr and 1.0 yr, respectively, and therefore of a similar magnitude to the average travel time towards the equator. Therefore what matters is, not only the extent of a certain methyl halide producing ecosystem, but also its geographical location. Given that the overall sizes of ecosystems are highly uncertain the geographical locations of these ecosystems must be even more so.

The work of Rhew et al. [2000], Yokouchi et al. [2000] and Keppler et al. [2000] supplied new data on possibly significant global methyl halide sources as well as identifying possible factors driving them [Rhew et al., 2000]. Since then these groups and others have supplied more measurement data on these and related sources. Nevertheless, the amount of data on methyl halide emissions from the various sources remains sparse, especially in view of the potential heterogeneous nature of terrestrial ecosystems. This is true both spatially as well as temporally. Furthermore, later studies on salt marshes have reported different findings [Dimmer et al., 2001; Cox et al., 2004; Drewer et al., 2006; Manley et al., 2006; Wang et al., 2006] and identified other potential drivers than the one reported originally by Rhew et al. [2000]. For tropical ecosystems, direct flux measurement data are only available from Yokouchi and coworkers [Yokouchi et al., 2000, 2002, 2007], who almost exclusively concentrated on CH₃Cl alone. Also, potential abiotic methyl halide emissions from tropical leaf litter, as suggested by Hamilton et al. [2003] and Wishkerman et al. [2008] on the basis of laboratory studies, have

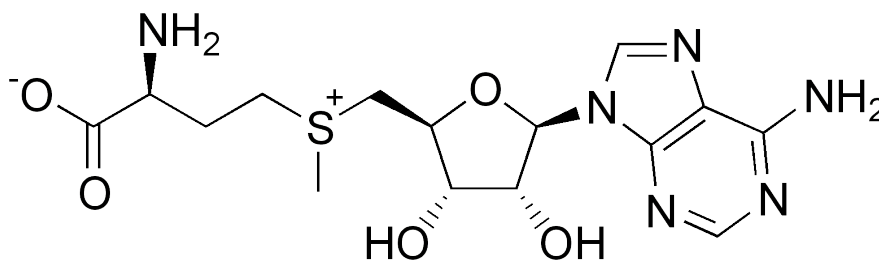


Figure 1.2: Chemical structure of SAM. The transferable methyl group is bound to the nucleophilic sulfonium ion in the centre of the structure [Nelson and Cox, 2001]. Picture taken from: http://en.wikipedia.org/wiki/S-Adenosyl_methionine

not been compared with field measurements in the tropics but only in temperate forests for CH_3Br alone [Drewer et al., 2008]. Apart from the latter study, publications have only touched upon the topic of emissions from temperate forests [Dimmer et al., 2001; Cox et al., 2004]. The state of data from these three sources is therefore currently unsatisfactory.

1.4 Cellular-level production of methyl halides

Some research has also focused on the cellular-level production mechanisms of methyl halides in plants and fungi. The review papers by Manley [2002] and Watling and Harper [1998] are good sources on these respective topics. To date it appears certain that methyl halide production in plants is affected by S-adenosyl methionine (SAM)-dependent methyl transferase activity [Saini et al., 1995; Manley, 2002] (Figure 1.2). However the enzymes responsible appear not to have a high affinity for halide ions as substrate; instead methylation of halide ions is likely an ‘accident’ caused by their ubiquitous occurrence in cell tissue.

In fungi, CH_3Cl has been identified as a possible primary metabolite used as an extracellular methylating agent for the breakdown of lignin used as a substrate by wood-rotting fungi [Watling and Harper, 1998]. The apparent methyl donor for CH_3Cl production can be either L- or D-methionine. Emissions of CH_3Cl again seem to be accidental, caused by a breakdown in the coordination of CH_3Cl -producing and CH_3Cl -consuming processes. Fungi grown on cellulose-based media can convert over 90 % of supplied chloride ions into CH_3Cl [Watling and Harper, 1998]; however most of this is not released into the atmosphere but used in further metabolic reactions. It is therefore the accidental release in certain growth stages of fungi that is the limiting factor of CH_3Cl emissions rather than the speed of production. It was also suggested that CH_3Br is not a significant product of fungal growth due to the generally low bromine concentrations in terrestrial ecosystems. However, both in plants and fungi, methylation of bromine was favoured over chlorine [Attieh et al., 1995; Saini et al.,

1995; Watling and Harper, 1998] partially compensating the lower natural abundance of the former.

Despite the profound knowledge of cellular-level reactions in plants and fungi the gap between the microscopic, cellular level, and the macroscopic ecosystem level remain to be bridged. However it does seem reasonable to suggest that the potential magnitude of methyl halide emissions from a particular ecosystem depends on the size of carbon stocks, both living and dead, as well as the abundance of the respective halogens in it. Forested areas and salt marshes are, by their respective merit of either large carbon pools or an abundance of bromine and chlorine, potentially the largest terrestrial sources globally for CH_3Br and CH_3Cl . For this reason this study examined emissions from these two ecosystems and attempted to identify possible drivers. The study sites were two salt marshes and three temperate forests in Scotland, and a tropical rainforest in Borneo, Malaysia. Work relating to the aforementioned issue of scarce ancillary data, such as geographical information of the extent and location of these three types of ecosystems in a global context were beyond the scope of this study, and were not addressed.

1.5 Overall aims

The primary aim of this study was the quantification of net fluxes of methyl halides in the natural environment, with the secondary aim of characterisation of these fluxes where possible. To this end, both observational monitoring studies, as well as controlled field, greenhouse and laboratory studies, were carried out over a period of 2 years in Scotland, and for 2 months in Borneo, Malaysia. The characterisation of fluxes was made in order to predict possible future changes of flux magnitudes due to (anthropogenic) climate variations. Measurements focused on salt marshes (Scotland) and forests (Scotland & Borneo).

1.6 Thesis layout

The remainder of this thesis is laid out thematically in four chapters: Chapter 2 discusses the general gas analysis and field equipment and issues regarding quality control and statistics. Chapter 3 discusses both the literature, special methods and results for methyl halide fluxes in salt marshes. Chapter 4 discusses work conducted in temperate forests and Chapter 5 work conducted in tropical rainforests. A comparison between the different studied biota and a final conclusion is given in Chapter 6.

Chapter 2

General Methodology

In this chapter the general methods that were used throughout the project are described. The chapter starts with methyl halide flux analysis in logical order, presenting background information when necessary, and then progresses to other general methods and finally to the statistical treatment of the results. Methods that are only relevant to particular parts of the project are discussed in the respective chapters.

2.1 Static enclosure systems and field monitoring

The most important part of this PhD project was the measurement of CH_3Br and CH_3Cl fluxes. In order to carry out this work, samples of interest had to be enclosed for a predetermined time and then gas samples taken. The way this was done concurrently with other measurements was important for the later interpretation of the resulting data, and therefore great consideration went into the enclosure design.

2.1.1 Enclosure designs

In choosing a suitable enclosure system for the experiment several aspects needed to be considered. Firstly the chamber had to avoid where possible any alteration to the plants' response, ideally achieving a natural behaviour of the studied object. Secondly it had to achieve reproducible conditions, and had to concentrate the analytes inside to such concentrations that samples taken could be analysed by the available analytical equipment. Thirdly, the enclosure system had to be user friendly. This means that it had to be easily built, be mobile, light, robust, inexpensive and easy to use, and allow the experimenter to monitor the conditions inside. Following these considerations the first and most important choice was between a static or a dynamic enclosure design.

A static enclosure has no gas exchange with the outside and can therefore be described as a “closed” box. A dynamic enclosure is an enclosure that provides forced air exchange with the outside, and therefore mimics more closely the “open” atmosphere. For a practical example of the latter please see the methods section in Cox et al. [2004]. Both these definitions describe extremes since many static enclosure designs are, either by design or default, not completely air-tight, whilst dynamic enclosures can have very small or very large exchange rates. The benefit of a static enclosure is a rapid concentration build up and depletion of any gases produced or taken up in it as well as the fact that measuring a flux involves simply taking a before- and after- enclosure sample. It is therefore advantageous if small fluxes are to be measured and financial budget is limited. The main drawbacks are that these strong concentration changes can alter the behaviour of the subject under study, and a possible internal temperature increase due to the greenhouse effect. The main advantage of an ideal dynamic chamber is that neither concentrations nor temperature build up to such a degree that it might affect the subject under study. The main disadvantage is that it is technically more difficult to sample from such a chamber and that the concentration differences between the “before” and “after” samples are much smaller than for a static enclosure and therefore less suitable if small fluxes are to be determined.

Since the detection capabilities of the analytical equipment and the constrained budget were limiting factors the choice fell clearly for a static chamber. However some of the issues of static enclosures mentioned above had to be addressed and quantified by carefully designed experiments that measured the effect of elevated methyl halide concentration on the gas fluxes.

2.1.2 Specific design features of life plant enclosure chambers

Although the plant enclosures described hereafter do differ in some details they all have some main features in common. All chambers were constructed either from polyethylene terephthalate - cyclohexane dimethanol copolyester (PETG) or polycarbonate of either 0.5 mm or 1.0 mm thickness. As shown in Figure 2.1 the material is approximately 90 % transparent to radiation in the visible range. All of the enclosures were constructed by bending a thin sheet of the above-mentioned materials into a cylindrical shape (Figure 2.2). Several opaque plastic rings of the appropriate diameter were slipped over the cylinder so-formed and glued in place. Then the two joining ends of the sheet were fastened together by screws and glued to form an air-tight seal. One end of the cylinder was closed with a circular sheet of the same material and again glued in place to form an air-tight seal. The remaining open end of the cylinder was either lined with two rings of door-and-window-seal P-profile on the outside to produce a branch chamber or a flange of appropriate diameter was fixed

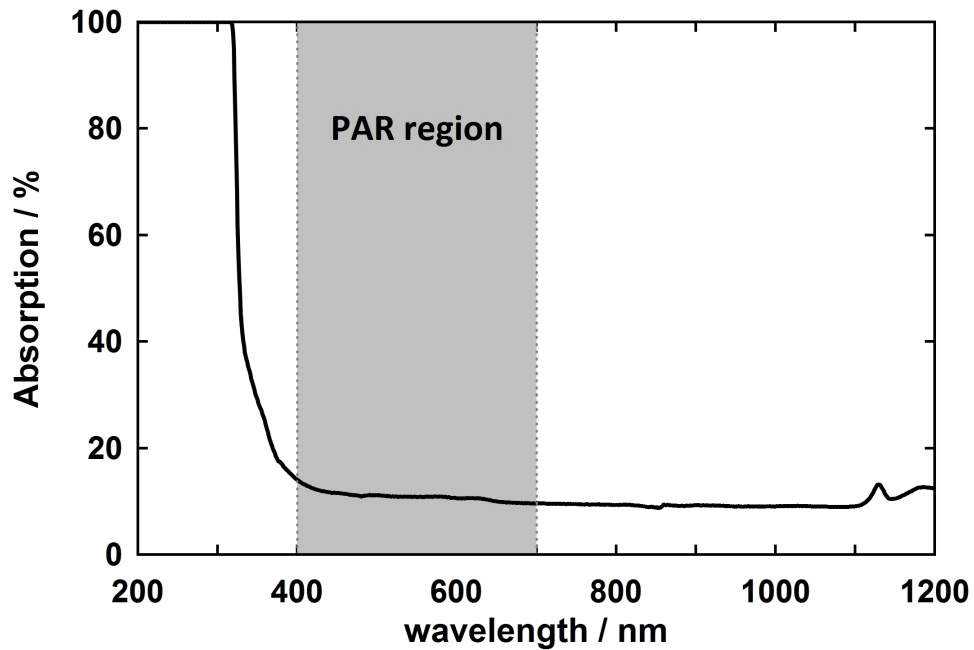


Figure 2.1: Absorption of radiation in the UV-Vis range by a 1 mm thick PETG sheet. The wavelength region between 400 and 700 nm is marked as photosynthetically-active radiation (PAR). Data were obtained by analysing a small piece of sheet material in a bench-top UV-Vis spectrometer (Lambda 900 UV-Vis/NIR Spectrometer, Perkin Elmer instruments, Norwalk, CT, USA).

to it to produce a ground chamber. Branch chambers were also fitted on their cylindrical wall with a polycarbonate socket with a 1/4 " - 20 UNC screw thread for mounting on a camera tripod. Where necessary, joints were sealed with silicone sealant. The dimensions of enclosures produced in this way ranged from the largest ground chamber being 40 cm in diameter and 1 m in length to the smallest branch chamber measuring 25 cm in diameter and 52.5 cm in length. All enclosures also featured two separate openings that were used to draw gas samples and to monitor inside air temperature via a data-logger. The sampling port consisted of an 8 mm diameter hole, that was lined with an 8 mm grommet through which a 1 mL disposable syringe was fitted. The plunger of the outward-facing syringe had been removed and the tip was connected with a silicone tube to a three-way tap (Discofix-2, Braun Melsungen AG, Melsungen, Germany). The temperature monitoring port consisted of a 6 mm hole, fitted with a 6 mm grommet. The temperature sensor was pushed through this opening during the measurements and formed an air-tight seal with the grommet. All chambers also featured forced air circulation to avoid any local concentration build-up inside the chamber which could affect both plant behaviour and representability of the gas sample drawn. The fans employed for this purpose varied in size and position according to the chamber size but all were powered from the outside by 12 V lead-acid batteries. Two examples of the most used chambers designs are shown in Figure 2.3.

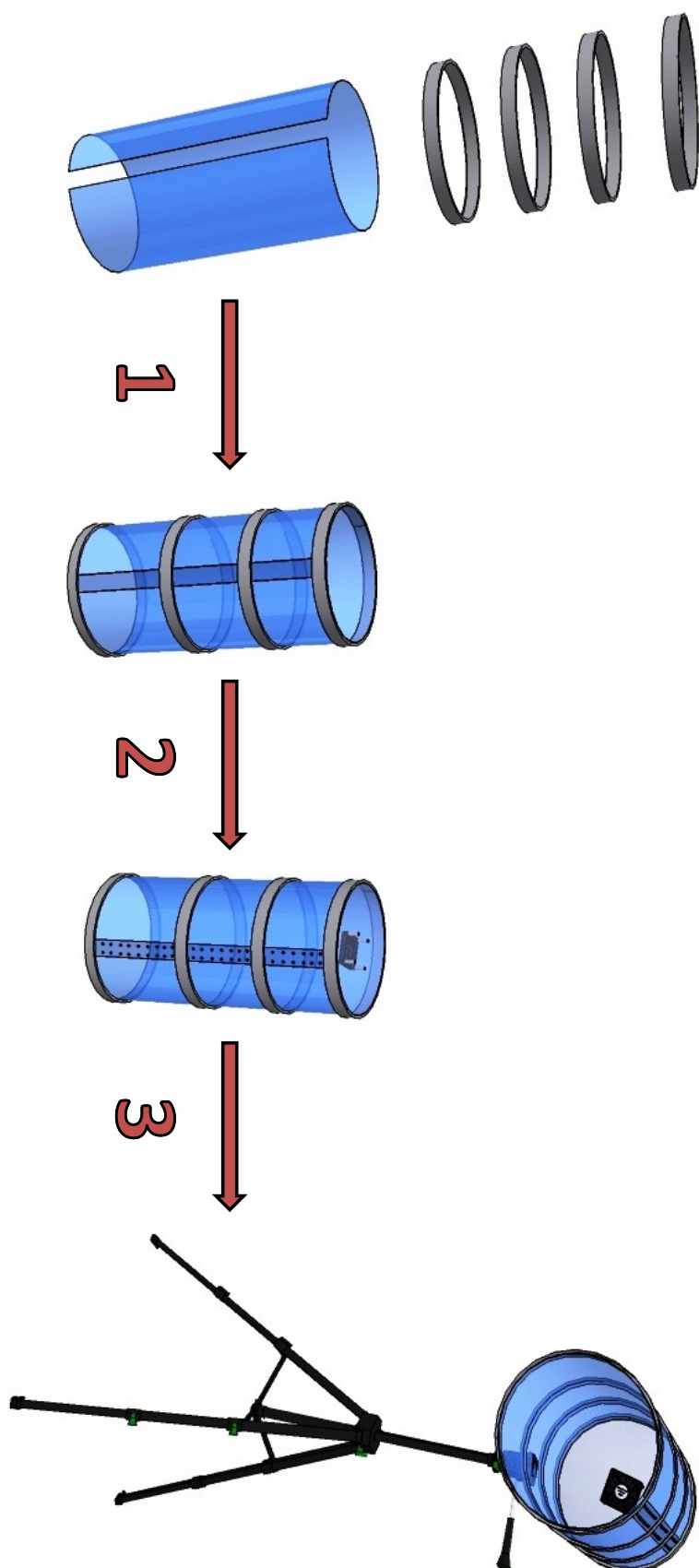


Figure 2.2: Production steps of a branch chamber from left to right. The first step shown is bending a thin PETG-co-polyester sheet into a cylinder, slipping the rings over the cylinder to keep the sheet in place and then gluing the two ends of the sheet together. In the second stage the previously glued joints are secured with screws and one side of the cylinder is closed with a circular sheet and an electric fan is installed. The last step is cutting out the sampling port and temperature port and finally the installation of a tripod mount.



(a) Branch chamber design used in Borneo. The enclosure here has length 80 cm, diameter 32.5 cm.



(b) Ground chamber design as used for salt marsh studies. The enclosure here has height 21.5 cm, diameter 40 cm.

Figure 2.3: The two chamber designs used for most field enclosure experiments. In both photos the sampling and the temperature port are visible.

2.1.3 Leaf litter enclosure chambers

For leaf litter enclosures a simpler design was chosen. Since leaf litter enclosures were conducted over longer periods of time—lasting hours rather than minutes—portability and air-tightness were of higher priority. Also the number of enclosures needed was greater since normally three or more enclosures were conducted concurrently, however no monitoring of sunlight was required. Therefore a simple more cost effective design was deemed appropriate. Also most leaf litter experiments were conducted in shaded areas so inside air temperature needed less close monitoring. The design chosen was a 12 L bucket made of opaque polypropylene with a tightly closing lid. The sampling port was made as described before from a 1 mL disposable syringe fitted through an 8 mm hole with grommet in the enclosure lid and connected with a silicone tube to a three-way tap. However no temperature monitoring port was installed. Instead, where temperatures were monitored online, this was done by placing a small temperature data-logger (UA-001-64 Temperature Pendant Data Logger, Onset Computer Corporation, Bourne MA, USA) inside the blank enclosure placed with the other sampling enclosures.

2.1.4 Environmental monitoring

One of the most controversial issues regarding methyl halide flux estimates of living plants has been, and remains, the influence of environmental factors on the emission and uptake of these gases by plants. In order to address this issue properly all possible drivers were monitored during the enclosure period.

During each live plant enclosure experiment the photosynthetically-active radiation (PAR), total solar radiation and the inner chamber temperature were electronically monitored (sampling rate: 2 seconds) via a small weather station (H21-002 Hobo Micro Station Data Logger, Onset Computer Corporation, Bourne MA, USA). The PAR sensor (S-LIA-M003 Photosynthetic Light Smart Sensor, Onset Computer Corporation, Bourne MA, USA) and total solar radiation sensor (S-LIB-M003 Solar Radiation Sensor, Onset Computer Corporation, Bourne MA, USA) were mounted level on a tripod at the same height as the vegetation inside the enclosure. The data-logger also recorded the start and end of the enclosure period via a voltage sensor (S-VIA-CM14 12-bit Voltage Input Adapter, Onset Computer Corporation, Bourne MA, USA) that was connected to a electric circuit which could be opened or closed by the operator with a switch. The inner chamber temperature was recorded by a stainless steel temperature probe (S-TMB-M002 12-Bit Temp Smart Sensor, Onset Computer Corporation, Bourne MA, USA) which was inserted into the monitoring port of the chamber mentioned above.

2.1.5 Sample retrieval in the field

Samples taken during field measurements were normally collected with a 1 L acrylic gas syringe (1000MAR-LL-GT, SGE Analytical Science Pty Ltd, Ringwood, VIC, Australia) with three-way tap and then stored in air sample bags. Most of these bags were 1 L Tedlar (polyvinyl fluoride) bags with polypropylene valves (232-01, SKC Inc., Eighty Four, Pa, USA) but some bags were 2 L Cali-5-bond bags (Calibrated Instruments Inc., Hawthorne, NY, USA) with either a plastic two-way tap or a metal valve and a three-way tap or 1.5 L Teflon-FEP (fluorinated ethylene propylene) bags with 1/4" polytetrafluoroethylene (PTFE) Spigot on/off tap valve connector (Scotland Adtech Polymer Engineering Ltd., Lochgelly, UK) and three-way tap. The estimated gas sample volume typically ranged from 500 mL to 700 mL. Once filled, the sample bags were stored in darkness until analysis. Storage times were kept to a minimum and were typically a few days and no more than one week for gas samples collected in Scotland. However, some samples from Borneo had to be shipped to Britain for analysis and therefore storage times were up to two weeks.

2.1.6 Gross and net fluxes

Due to the nature of the experimental design all fluxes measured from the salt marsh enclosures are essentially net fluxes. This means that for example methyl halide emissions from a salt marsh collar can be either the result of gross emissions from the plants inside the collar alone or the result of a combination of individual emissions and uptake reactions, e.g. by soil micro-organism. Since there is inherently no possibility to separate out the different contributors to a net flux in one enclosure experiment, other ways such as the exclusion of one or more possible contributors conducted over several enclosure experiments have to be found. However, branch and litter enclosures only comprised the plant material itself and chamber effects were accounted for by subtraction of blank samples. Similarly, for the greenhouse study both chamber and soil effects were separated from the measured net fluxes to yield gross fluxes. To all intents and purposes the results from these enclosures represent the gross fluxes from these sample types.

2.2 Methyl halide analysis

2.2.1 Overview of analytical techniques for methyl halide detection

The history of methyl halide analysis is closely linked to the development of the gas chromatograph (GC) and, even more important, its associated detectors. To date, these systems are the most widely—if not the only—analytical equipment used to measure minute concentrations (parts per billion (10^{-9}) by volume (ppbV) to parts per quadrillion (10^{-15}) by volume (ppqV)) of many important gases such as halogenated hydrocarbons, NO_2 , SF_6 and others. For this purpose the GC is normally coupled to either an electron capture detector (ECD) or a mass spectrometer (MS). However, a recent example using the less sensitive flame ionisation detector (FID) has been reported [Saito et al., 2008].

Most modern systems feature 3 main components:

1. Pre-concentration unit: used to pre-concentrate analyte, reduce sample volume, eliminate matrix components and rapidly inject sample onto column
2. GC with capillary column: separation of the different sample constituents
3. ECD or MS: detection and characterisation of sample constituents

Pre-concentration units are in the widest sense cryogenic traps. The main purpose is to reduce the sample volumes from up to several litres to less than a mL for the application to capillary columns. They also enable the rapid injection of the pre-concentrated sample onto the GC-column via resistive heating. This is of particular importance for the resulting chromatographic peak that would otherwise be distorted or unnecessarily broadened. Pre-concentration units are often custom made from steel tubing filled with solid adsorbent such as Tenax or Carbotrap or glass beads [Rhew and Abel, 2007; Rhew et al., 2007; Redeker et al., 2003; Saito and Yokouchi, 2008; Saito et al., 2006]. However the use of micro-traps which are comparable to GC-capillary-columns with very small volumes has also been reported [Rhew et al., 2001; Huang et al., 2000; Prinn et al., 2000; Worton et al., 2008]. Micro-traps have the advantage of very tight temperature control and reduced dead volumes but are sensitive to excess sample moisture, so often a Nafion dryer [Prinn et al., 2000; Mangani et al., 2003; Worton et al., 2008] or equivalent method is installed upstream. For cooling purposes, either cryogenic materials such as ice [Redeker and Cicerone, 2004], solid CO_2 [Huang et al., 2000] or liquid N_2 [Rhew and Abel, 2007; Rhew et al., 2007; Redeker et al., 2003; Rhew et al., 2001; Saito et al., 2006], Peltier cells [Prinn et al., 2000; Worton et al., 2008] or even Stirling motors [Saito and Yokouchi, 2008] have been used. The rapid heating required for on-column injection is achieved by resistive heating either of the trap itself [Prinn et al., 2000] or of heating wires wrapped around it [Saito and Yokouchi, 2008] or by reversing the

Peltier-cooling [Worton et al., 2008]. In some instances the GC-column itself has been used to trap the analyte at cryogenic temperatures at the column head and then been heated by the GC-oven to start the chromatographic process [Harper et al., 1999; Saito et al., 2006].

Most GC columns used are capillary columns with typical diameters of 0.15–1 mm and lengths between 10–105 m rolled up into a coil inside the GC oven [Rhew and Abel, 2007; Rhew et al., 2007; Redeker et al., 2004, 2003; Huang et al., 2000; Prinn et al., 2000; Harper et al., 1999; Saito and Yokouchi, 2008; Saito et al., 2006; Worton et al., 2008]. These extreme lengths give capillary columns superior separation capabilities which cannot be matched by packed columns. Most modern analytical procedures make use of temperature programs starting at lower temperatures and then raising them at a constant rate to a final steady temperature [Prinn et al., 2000; Harper et al., 1999; Saito et al., 2006; Worton et al., 2008]. This common technique is useful for separating samples containing constituents with a wide range of boiling points. However, the use of an isothermal GC technique has been reported [Redeker et al., 2004].

The first of the two main detectors for methyl halide analysis is the ECD which can be either used in its normal form [Redeker and Cicerone, 2004; Redeker et al., 2004, 2003] or with oxygen doping for more sensitivity towards weakly electron absorbing compounds [White et al., 2005; Rhew et al., 2001; Huang et al., 2000]. The information obtained from a GC-ECD is essentially 2-dimensional: Identification is achieved by a known retention time and quantification by the peak area at this retention time.

In the second main detection technique an MS-instrument ionises the GC effluent in one of various ways, the most widely used being electron-impact ionisation (EI) [Prinn et al., 2000; Worton et al., 2008] and, in a recent example, by negative ion chemical ionisation (NICI) [Worton et al., 2008]. The former produces positive ion fragments of the sample whilst the latter produces almost un-fragmented negative ions. Many machines are capable of switching between the two modes to exploit the different sensitivities of each to different compound classes. The resulting ions are then separated in a drift tube by a mass-to-charge ratio (m/z)-selective process, very often a quadrupole [Rhew and Abel, 2007; Rhew et al., 2007; Redeker et al., 2003; Prinn et al., 2000; Harper et al., 1999], to selectively channel ions of a specific m/z value towards the mass selective detector (MSD). The data obtained from a GC-MS are 3-dimensional: identification can be achieved by both the retention time as well as the mass of either fragments or ions. This enables the identification of a compound without the need for a calibration standard, whilst quantification is achieved by the intensity of a pre-calibrated m/z . To achieve higher sensitivities towards pre-calibrated compounds GC-MS instruments are often run in selected ion monitoring (SIM)-mode rather than scanning the full mass spectrum [Rhew and Abel, 2007; Rhew et al., 2007; Redeker et al.,

2003; Prinn et al., 2000; Harper et al., 1999; Saito et al., 2006; Worton et al., 2008]. Although this reduces the information obtained, it is advantageous for routine work where the target compounds and their fragmentation patterns are known and the MS detector is primarily used to distinguish more accurately between analyte and interference signals. Another advantage of GC-MS is the possibility to use isotopic markers, to de-convolute methyl halide net flux into separate uptake and production fluxes [Rhew and Abel, 2007]. A special form of mass spectrometer (MS), isotope ratio mass spectrometry (IRMS) is used to accurately measure $\delta^{13}\text{C}$ signatures [Harper et al., 1999, 2003; Saito and Yokouchi, 2008] for different global sources and sinks therefore helping to constrain the overall budget.

Although becoming superseded by GC-MS techniques GC-ECDs are considerably cheaper in both primary acquisition and running costs and therefore are still widely used.

2.2.2 Current GC equipment

The gas samples collected in the field were analysed on a GC with front-end pre-concentration unit and ECD (scheme in Figure 2.4). The pre-concentration unit consisted of two parts. The

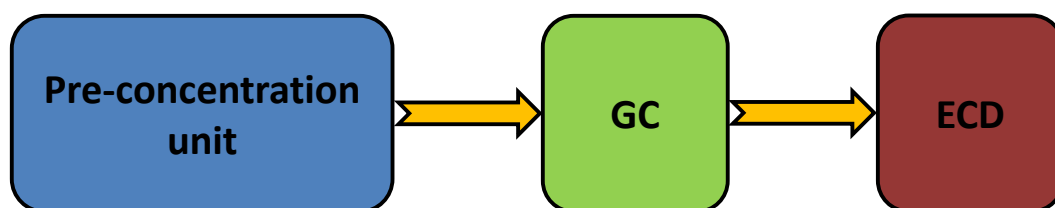


Figure 2.4: Diagram of methyl halide analysis. In the pre-concentration unit the samples are separated from its main matrix components and pre-concentrated. In the GC itself the remaining sample components are separated and then detected by the ECD.

first part was an absorbent trap made of a 1/4 inch stainless steel tube filled with ~0.6 g Tenax-TA 60/80 absorbent polymer that was held in place inside the tube with silylated glass-wool stoppers at both ends. The trap was cooled electrically with two pairs of stacked Peltier cells (Figure 2.5). One cell of each pair was a 3.4 cm × 3 cm, 28.7 W Peltier cell (HT6-7-30-RTV, Melcor Corporation, Trenton NJ, USA), connected on its cooling side to a metal body that embraced the absorbent trap. On its heating side it was in thermal contact with a 4 cm × 4 cm, 1.5 mm thick aluminium plate which in turn was in contact to the cooling side of a 4.4 cm × 4 cm, 72 W Peltier cell (HT8-12-40-RTV, Melcor Corporation, Trenton NJ, USA). This cell was in thermal contact on its heating side with an aluminium heat exchanger. The heat exchanger was fed with a water:ethylene glycol mixture (1:1) at -5°C from a constant-temperature circulator (Polystat constant temperature circulator, Cole-

Parmer Instrument Company, Vernon Hills, IL, USA). All thermal contacts inside the Peltier assembly were achieved with silicone thermal conduct paste. The absorbent trap itself was wrapped in electrically insulated heating wires that enabled the tube to be heated up via resistive heating.

The second part of the pre-concentration unit was a cryogenic trap which consisted of a 20 cm long 1/8 inch diameter stainless steel loop filled with 0.1 mm diameter glass beads (BioSpec Products Inc., Bartlesville, OK, USA). Cooling was achieved by submersion into a dry ice bath at -78°C . Again, this tube was wrapped in electrically insulated heating wires to allow for rapid resistive heating. The two parts of the pre-concentration trap were connected with each other and the GC with 1/16 inch diameter stainless steel tubes. Switching between load and inject positions for both traps was achieved with two 6-port two-position valves (Valco Incorporated, Figure 2.6). The pre-concentration system was controlled via a PC.

The GC unit consisted of an HP 5980 gas chromatograph with a 30-metre long, 0.32 mm inner diameter DB624 capillary column (J&W Scientific). The temperature program was set up as 5 min at 40°C , then ramping at $40^{\circ}\text{C min}^{-1}$ to 240°C and holding for 5 min. The carrier gas was an argon methane mixture (90 % argon, 10 % methane) whilst the ECD make-up gas was a mixture of $\sim 0.2\%$ O_2 in N_2 . After leaving the column the analyte passed through to the ECD where it was detected and quantified.

For analysis, 100 mL of gas sample was injected into the electrically-cooled absorbent trap at a temperature between -26°C to -30°C (Figure 2.6a). All gases whose boiling point was lower than the trap temperature were not retained but flushed out with the carrier gas stream. The first valve was switched into inject mode and the trap was heated to 150°C (Figure 2.6b). The sample was transferred with the carrier gas at a flow rate of 15 mL min^{-1} into the cryogenic trap which was cooled to -78°C with dry ice. Again all gases which were not retained were flushed out of the vent, further concentrating the analyte. The cryogenic trap was then heated rapidly to 180°C and the sample was flushed by the carrier gas into the GC (Figure 2.6c).

The flow rate of the carrier gas through the capillary column was $\sim 1.3\text{ mL min}^{-1}$. When the sample reached the ECD it was made up with a 2 % O_2 in N_2 gas mixture with a flow rate of 3 mL min^{-1} , and a separate N_2 gas stream of $\sim 30\text{ mL min}^{-1}$. The resulting chromatogram was recorded by a PC using TurboChrom[®] software and the peak areas for the methyl halide peaks were integrated manually on the computer (Figure 2.7).

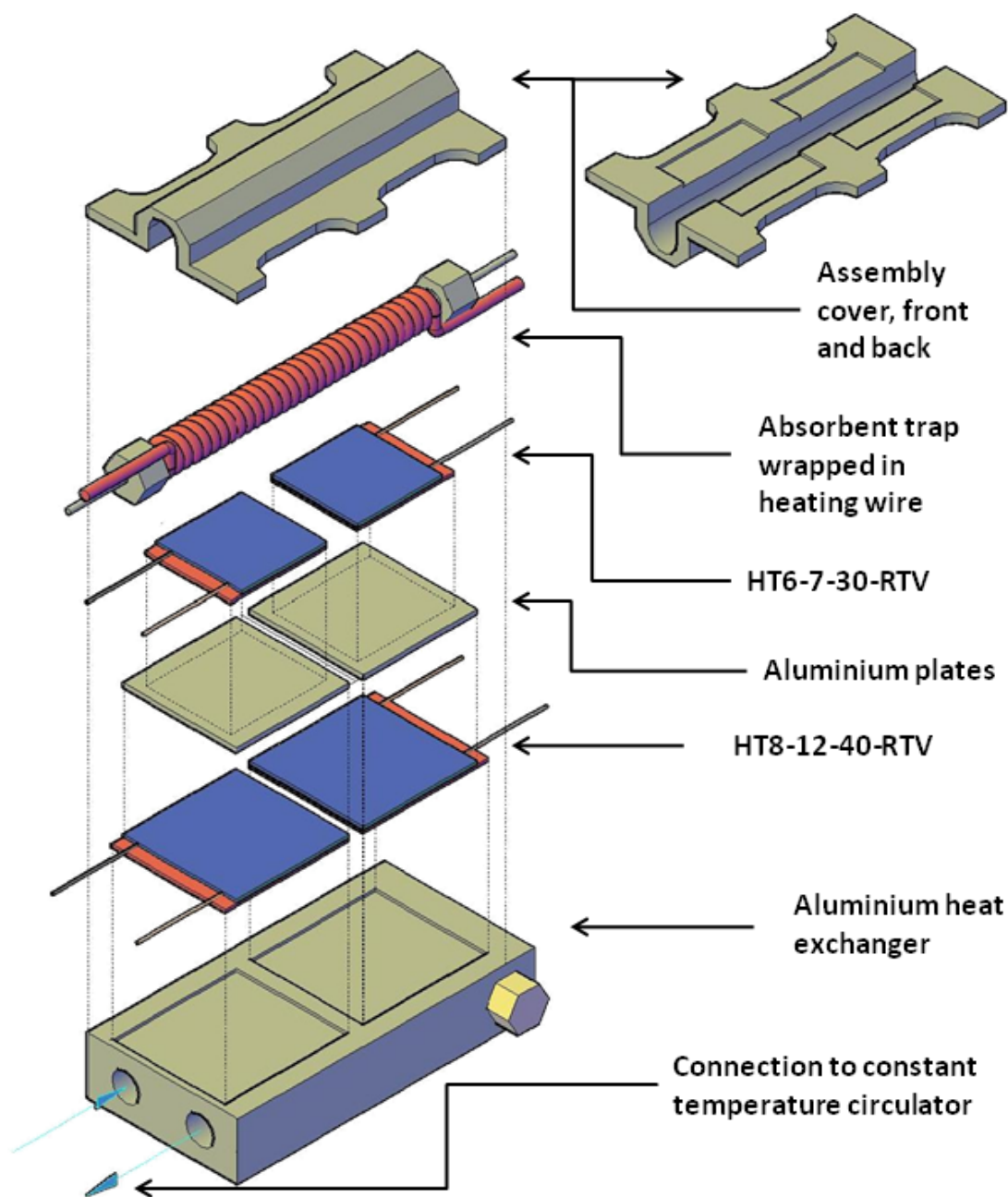
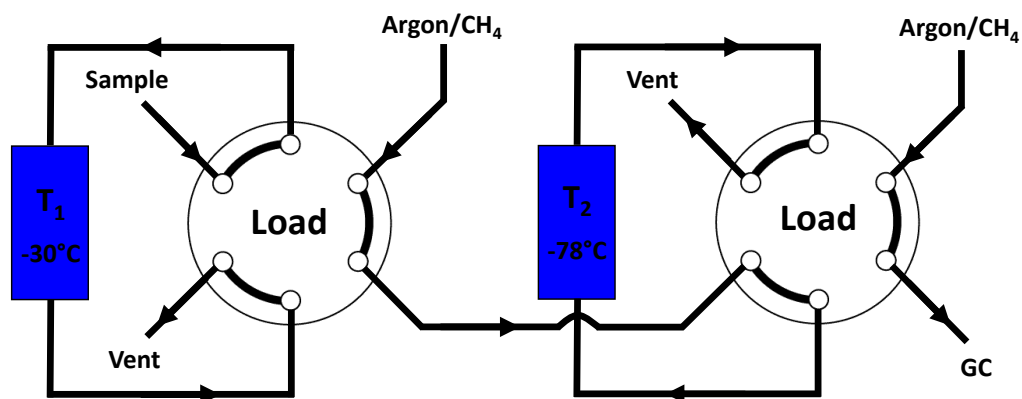
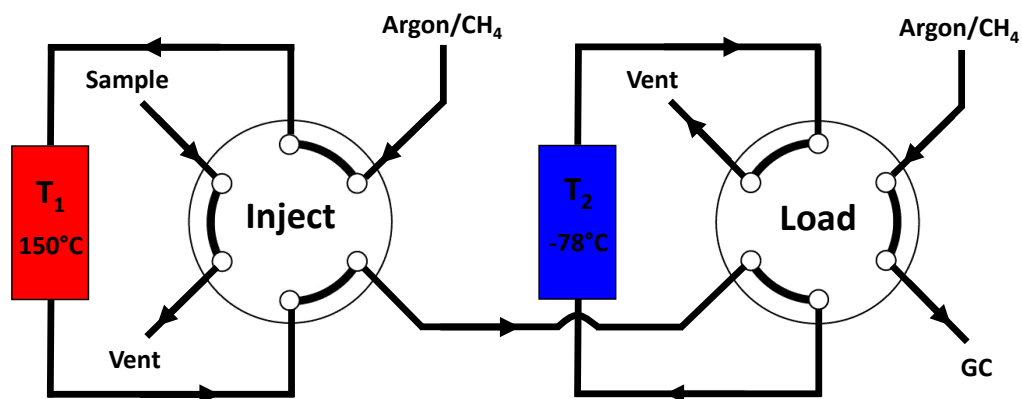


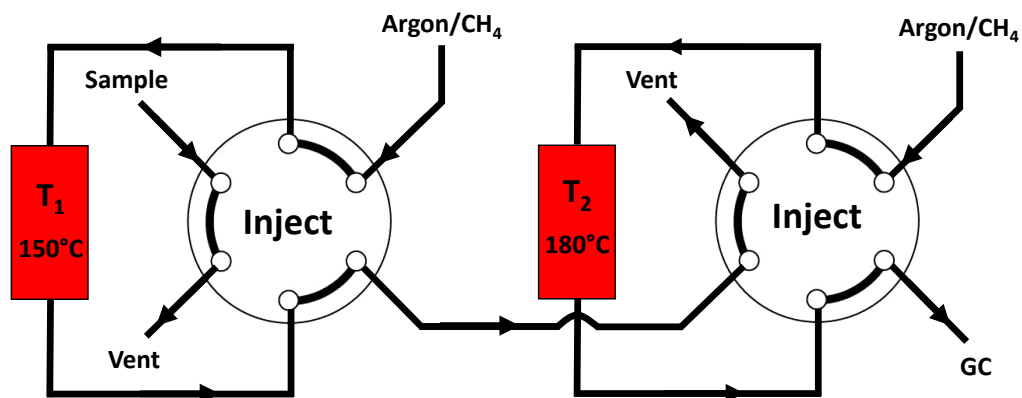
Figure 2.5: Exploded view of absorbent trap assembly drawn to scale. Shown from bottom to top are the aluminium cooling block, the 44×40 mm Peltier cells, the aluminium plates, the 34×30 mm Peltier cells, the absorbent trap housing containing the Tenax-TA 60/80 with the connecting nuts to the smaller bore gas plumbing and the assembly cover shown from both sides. The main purpose of the cover is to hold the whole assembly together and to ensure best possible cooling of the trap housing from all sides. Not shown are 6 Nylon screws connecting the cover with the cooling block. They are positioned at the 'side wings' of the cover.



(a) Position 1: Both traps are cooled and in load position. Sample is injected into trap 1.



(b) Position 2: Trap 1 has switched from load to inject position and is electrically heated to 150°C . The pre-concentrated sample is transferred into trap 2.



(c) Position 3: Trap 2 switches to inject position and is electrically heated to 180°C . The sample is quickly transferred into the GC.

Figure 2.6: Operation cycle of pre-concentration unit. Shown in the diagrams are trap 1 and trap 2 as rectangles T_1 and T_2 on the left and right respectively. The two valves are represented by large circles with the six inlet/outlet ports shown as smaller circles. Gas pipes are drawn as thick black lines with arrows indicating the flow path.

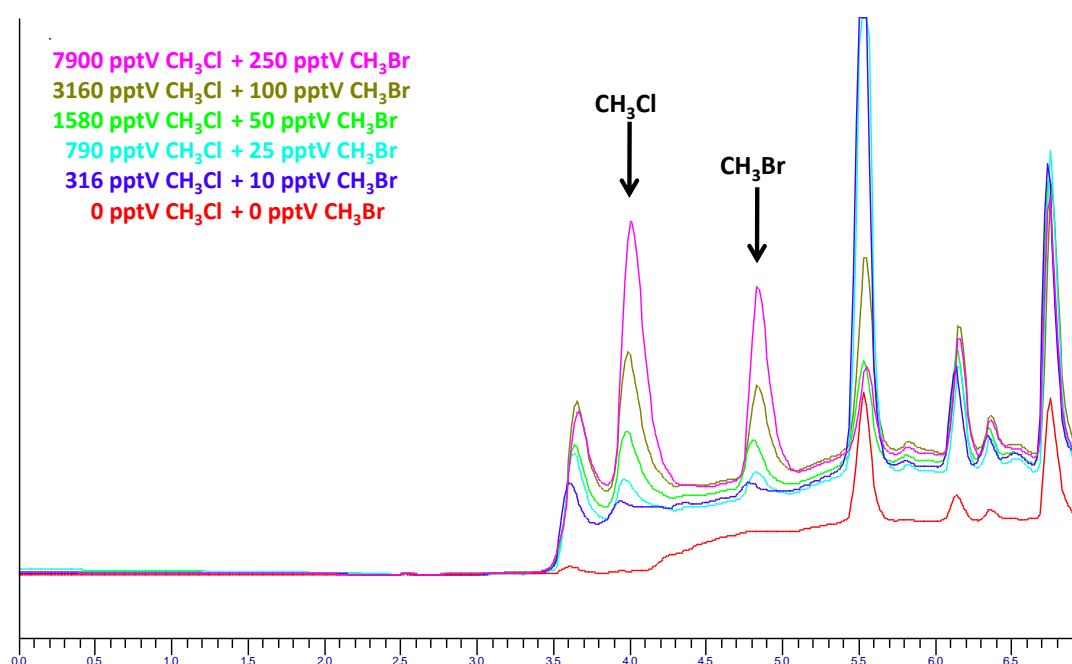


Figure 2.7: Chromatograms from the 11/08/2008 showing overlay of calibration standards. The difference in baseline between calibration blank and the rest of the standards is most likely due to impurities in the two primary CH_3Br and CH_3Cl standards that were diluted to make up the calibration standards.

2.2.3 Previous trapping system and modifications undertaken to it in this work

The previous absorbent trap cooling system established by Julia Drewer was insufficient for the analysis of CH_3Cl since the absorbent trap could not be cooled to a temperature low enough to ensure quantitative adsorption of the compound [Drewer, 2007]. This section explains the operational principle of Peltier cells, and describes the steps undertaken in this work to replace the previous set-up with a more sophisticated arrangement.

Peltier cells are thermoelectric devices that operate via the reversed Seebeck effect. If two dissimilar metals are joined together at two junctions to give a closed circuit and the two junctions are held at different temperatures then an electromagnetic potential, proportional to the temperature difference is established and a current starts to flow. In reverse, if two junctions of two dissimilar metals are subjected to an electric potential then a temperature difference proportional to the potential applied is established between the two junctions, i.e. one side starts to cool down whilst the other heats up. In a Peltier cell several such junctions made from selenium- and antimony- doped bismuth-telluride are connected electrically in series and thermally in parallel and integrated into modules (Figure 2.8). Peltier cells have several advantages: no moving parts, can take any orientation, low cost, and precise

temperature control when used in conjunction with a thermocouple [Laird Technologies PLC, 2009].

Before the modifications were made, the two Peltier cells sat with their heating side on an aluminium block that was hollowed out by bores which were connected to a water tap. The tap water would therefore cool the cooling block and thus also the hot side of the Peltier cells. The Peltier cells on their cooling side were in thermal contact with a thin metal plate that was in turn in thermal contact with the absorbent trap. The trap was held in place by a second metal plate opposite the first, which was screwed in place on the

metal cooling block. This arrangement had four major flaws: firstly, the temperature of the cooling block that was meant to keep the Peltier cells cold could not be controlled; secondly, a Peltier cell is only able to produce a certain temperature difference between its warm and its cold side, in this case $\sim 67^{\circ}\text{C}$. However this maximum temperature difference is only achieved when no load is applied, i.e. if the Peltier cell is not cooling anything but itself. This meant in practical terms that the Peltier cells would not be able to achieve the temperature difference of $\sim 40^{\circ}\text{C}$ between the tap water and the -30°C required for the absorbent trap. Thirdly, the thermal contact between the Peltier cells and the absorbent trap was deemed insufficient since it was only cooled from one side. The final flaw was that the whole assembly was poorly insulated which meant that a lot of the cooling power was lost to the environment and that during the cooling cycle ice would accumulate on the cold surface and then melt during the next heating cycle thereby leaving a pool of water near electrical equipment.

In order to achieve the desired working for trapping CH_3Cl several modifications had to be made. First of all, the tap-water feed was replaced with a constant temperature circulator that could itself establish sub-zero temperatures for the cooling medium and pump a freeze resistant liquid through the cooling block. Secondly the cooling block was replaced with a new model in which 1 mm deep grooves in the shape of the Peltier cells were inserted. This provided better thermal contact and also stopped the Peltier cells from “wandering around” during assembly. Thirdly, the two old cells were replaced by two more powerful ones and then two further, smaller cells were stacked on top of these with small aluminium plates to provide

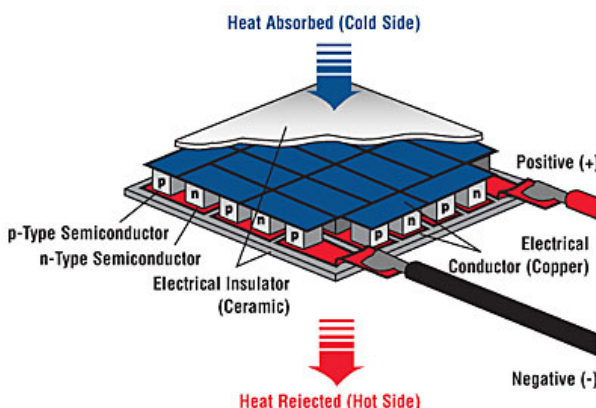


Figure 2.8: Cutaway drawing of modern Peltier cell. Taken from “Thermoelectric Handbook”, Laird Technologies PLC, <http://www.melcor.com>.

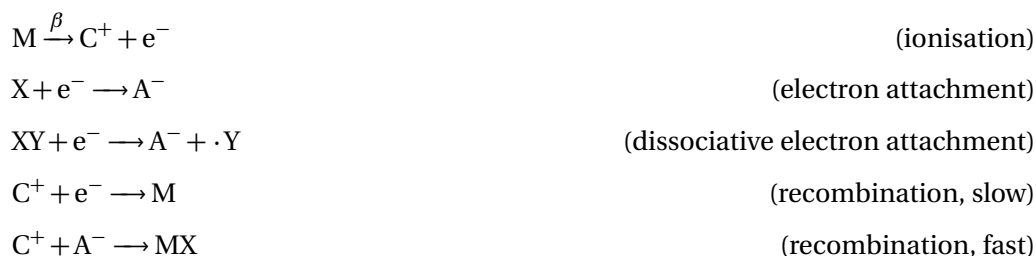
better thermal contact. This resulted in the theoretical temperature difference being doubled to $\sim 120^\circ\text{C}$. Fourth, the absorbent trap was placed directly on top of the latter cells and held in place by a U-shaped metal block that ran parallel to the cooling block on its fringes. This U-shape was made to fit the absorbent trap exactly and also provided 1 mm deep grooves for the two smaller Peltier cells. It therefore held them in place and was in thermal contact with the Peltier cell assembly, providing cooling from all sides to the trap. Lastly, the whole cooling assembly was made with as little material as possible to reduce the load which the Peltier cells had to cool to a minimum and the whole assembly was placed within a block of polystyrene to provide adequate insulation. Overall these changes made it possible to achieve temperatures as low as -45°C compared to the few degrees below zero achievable beforehand.

2.2.4 Theory and operation of an electron capture detector

2.2.4.1 Introduction

The modification of the existing ECD was essential for large parts of the analytical work carried out in this study. However this work was purely operational, i.e. focused on the application of well-known methodologies to a particular analytical problem rather than exploring the underlying theory in full. This section gives a brief introduction into the quite complex field of electron capture and oxygen doping but does not claim to cover all theoretical details since this has not been the aim of this study.

2.2.4.2 Theory: Main reaction in an undoped ECD



M is a carrier gas molecule, C^+ a cation, X an electronegative atom, molecule or molecule group, Y the remainder and A^- an anion.

An ECD operates by irradiating a carrier gas with high energy electrons (β - particles) thereby ionising it, and producing a plasma of radicals, low energy electrons (thermal electrons) and cations. Since thermal electrons only very slowly recombine with the cations, the concentration of the former stays for all practical purposes unchanged. The plasma is then subjected to an electric potential which leads to the establishment of an electric current across the carrier gas. This current is stable as long as no electrons are removed from the gas by other constituents of the carrier gas. If however an electronegative compound such as NO_2 is present in the gas stream it captures some of the thermal electrons and rapidly recombines with the cations. This process depletes the gas stream of free electrons which leads to a decrease in detector current and can then be read out as a signal [Poole and Zlatkis, 1981].

2.2.4.3 Operation

A typical ECD (as used in this study) consists of a hollow stainless steel cylinder (housing) which also forms the cathode and is lined on the inside with a ^{63}Ni foil. The radioactive ^{63}Ni acts as β -particle source. Within the cylinder is placed a coaxial stainless steel anode (sensor). The carrier gas flowing in from the capillary column is diluted with make-up gas and travels through the ECD along the axis of the housing. By doing so it passes the ^{63}Ni , is ionised, and a current is established between cathode and anode.

There are several ways in which to operate an ECD and this report shall concentrate on the mode used by the equipment in this study: the pulse-modulated constant-current mode. When a static potential (i.e. a d.c. voltage) is applied to the plasma, the electrons travelling towards the anode have a different speed from the cations travelling towards the cathode. This causes the space charge effect: positive ions near the cathode increase in concentration and create a potential opposite the applied potential and therefore change the behaviour of the detector in complex and unfavourable ways. Another complicating factor is that a d.c. voltage causes both free electrons, and also anions produced by electron capture to be detected at the anode, without being able to distinguish between the two. Thus the signal of an electronegative compound occurring is diminished. If on the other hand the potential difference is only applied in pulses of short lengths, a thermal equilibrium is established.

Free electrons are relatively slow at recombining with cations to neutral molecules whilst the anions produced by electron capture very quickly recombine. If sufficient time is left between each pulse event only the free electrons but no anions are left in the gas stream, and the change in current measured during a voltage pulse reflects the difference of free electron concentration between a sample with and without a certain analyte concentration. However,

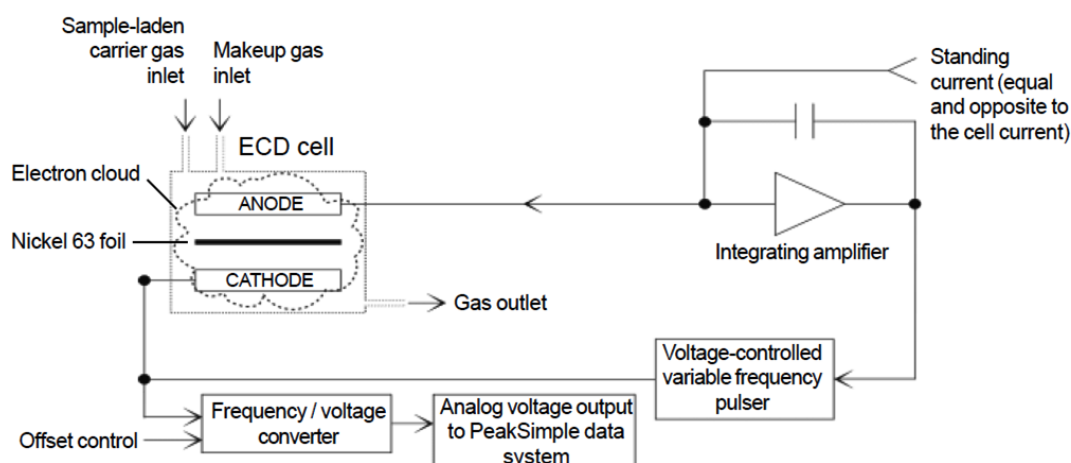


Figure 2.9: Schematic of an ECD operating in pulse-modulated constant-current mode. Taken from <http://www.srigc.com> - SRI Instruments

instead of measuring the change of current at a constant pulse rate, the pulse-modulated constant current ECD keeps the current at a constant value but modulates the pulse frequency instead; increasing the frequency if the current breaks down due to the occurrence of an analyte and decreasing the frequency if the current is above the reference current (Figure 2.9). The signal recorded by the detector is therefore not Amperes but Volts. This mode of operation both increases the range of linear detector response and reduces disturbance in detector operation due to interferences that are entering the detector. Temperatures inside the ECD are typically held at 300°C to 350°C, which reduces disturbances due to contamination from column bleeds and also enhances the sensitivity for CH_3Br as it undergoes dissociative electron attachment.

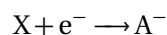
2.2.4.4 Oxygen doping theory

Electron capture detectors are exceptionally good at detecting and measuring minute quantities of halogen-containing compounds, which is also their main use today. However, not all halogenated organic materials are detected equally well. The GC system previously built-up by Julia Drewer had a lower limit of detection of approximately 10 pptV CH_3Br without any modifications to the ECD. However the same system was not capable of measuring CH_3Cl concentrations of 550 pptV, which is the background concentration in air; the main reason being a smaller thermal electron-attachment cross-section for Cl compared to Br. In order to address this issue a technique called oxygen doping was used. Oxygen doping describes the deliberate addition of small concentrations of O_2 to the make-up gas stream of the ECD. There the oxygen undergoes several reactions inside the detector that

are best described as electron-capture catalysis [Grimsrud and Miller, 1978; Grimsrud, 1981].



Therefore the overall reaction is:



Relevant reactions for oxygen doping: X is an electronegative atom, molecule or molecule group, and A⁻ an anion.

The reason that this catalytic reaction works (the oxygen nominally never changes its oxidation number) is that the equilibrium between O₂ and O₂⁻ is very much faster than any of the other reactions described earlier. The concentration of O₂⁻ can therefore be assumed constant since it will be reproduced almost instantly as it is consumed by electron transfer from the stock of O₂ in the gas stream. Furthermore the O₂⁻ catalyzed electron transfer described above is compound specific and more importantly specifically enhances the signal of otherwise weakly responding compounds.

2.2.4.5 Practical modifications

The practical work to achieve the effect of oxygen doping is very simple in principle. The make-up gas had to be changed from a 10 % CH₄/Ar mixture to a 0.2 % O₂/N₂ mixture [Grimsrud and Miller, 1978; Sturrock et al., 1995; Bassford et al., 1998]. This was done by mixing a commercial 2 % O₂/N₂ mixture with pure N₂ in a 1:10 ratio to a total flow rate of 30 mL min⁻¹. However the flow rate of the 2 % O₂/N₂ mixture was only 3 mL min⁻¹ and therefore very difficult to control with the available equipment. Furthermore the ECD is very sensitive to changes of conditions, especially oxygen levels in the make-up gas, and needed between days to weeks to “settle down”.

A second parameter that needed to be considered was the ECD temperature since this can both increase or decrease the detector response and the signal-to-noise ratio for each analyte individually. The effect of the ECD-temperature on both CH₃Br and CH₃Cl were investigated, but as reported in the literature, a lowering of temperature from 350 °C to 300 °C did not significantly increase the CH₃Cl response but did weaken the CH₃Br signal [Grimsrud and Miller, 1978], so the ECD temperature was left at 350 °C as before.

2.3 Other general methods

2.3.1 Determination of fresh weight, dry weight and water content

2.3.1.1 Soils

Soil samples were taken with an 8 cm long, 1.7 cm inner diameter corer and immediately placed in air-tight zipper-bags and stored in a fridge until further analysis. The soil material was freed of any large root or plant material and placed in pre-weighed tins. Masses of tin and wet soil were recorded and the samples dried in an oven at 105 °C to constant weight. To measure dry weight the soil samples were cooled to room temperature for 10 min in a desiccator before weighing.

2.3.1.2 Live plant material and leaf litter

Fresh weight of plant materials was recorded upon arrival in the laboratory. The leaves or leaf litter were put into paper bags and dried in an oven at 70 °C to constant weight. Plant matter and bag were weighed immediately on a balance without prior cooling; after final dry weight measurements the paper bag was emptied and reweighed.

All water content values given in this report, unless otherwise stated are expressed as % (w/w fresh weight), i.e. relative to the fresh sample weight and were calculated as follows:

$$\text{water content} = 100 \times \frac{\text{fresh weight (g)} - \text{dry weight (g)}}{\text{fresh weight (g)}}$$

2.3.2 Determination of total bromine and chlorine with XRF spectrometry

2.3.2.1 Theory

One great challenge for the characterisation of methyl halides is the correlation of methyl halide fluxes with halogen content of the relevant emitting materials or organisms. However most methods for the detection of halogen content rely on lengthy aqueous extraction techniques to bring the bromine and chlorine into solutions followed by ion chromatography. However this is both time consuming and imprecise since it has to be assumed that all

halogen is in water-extractable ionic form and that the extraction technique is essentially quantitative. Furthermore the final extracts from plant material include very high concentrations of macromolecular organic substances that could not be removed with available techniques and which risk damaging of the analytical equipment.

The X-ray fluorescence spectrometry was sparingly used in this project. The technique allows the non-destructive analysis of most metals and some heavier non-metals by irradiation of the sample with X-rays. An atom struck by an X-ray will transfer the absorbed energy to one of its innermost electrons thereby ejecting it from the core. However the excited atom is not stable and an electron from an outer shell rapidly ‘falls’ down into the vacant position, emitting an X-ray in the process. Since the energy transitions between the various inner/outer shell electrons are specific for each element, and the emission intensity can be correlated to the concentration in a sample, this technique offers a powerful tool for quantitative element-specific solid-state analysis.

2.3.2.2 Analysis

Plant and leaf litter material were analysed for both total chlorine and total bromine content on two custom-built X-ray fluorescence (XRF) machines. Since the analysis of the samples was carried out at the Technical University of Braunschweig, Germany and the University of Heidelberg, Germany by Dr. Benjamin S. Gilfedder and Dr. Andriy K. Cheburkin, respectively, the actual analytical process will only be broadly outlined.

Samples of either leaf litter or of a specific plant species were collected, ensuring that each sample was a mixture of randomly chosen sub-samples in the field, or in the case of greenhouse samples the whole vegetation of a pot. The fresh samples were washed with de-ionised water and dried with paper towels. The samples were then put into paper bags and dried at 70 °C to constant weight as described above. Once dried, the samples were stored in air-tight zipper-bags and shipped to Germany for analysis.

The machines used for XRF analysis were both energy-dispersive XRF spectrometers (EDX) specifically built for analysis of peat and plant samples. Bromine analysis was carried out on the EMMA-XRF in Braunschweig [Cheburkin and Shotyk, 1996] and combined total chlorine and bromine analysis on the TITAN-XRF in Heidelberg [Cheburkin and Shotyk, 2005]. Calibration of the machines was carried out with certified plant materials with known halogen content and analytical uncertainty estimated to be less than 10 %.

2.4 Data analysis, statistics and quality control

2.4.1 Literature sources and software used for data analysis and statistics

Statistical analysis of experimental results as outline below was routinely performed using either commercial software packages or formulae given in Miller and Miller [2005].

Correlation coefficients R (Pearson product moment correlation coefficient), linear regression fits and paired t -tests were calculated with Microsoft Excel[®] software. F -tests, and t -tests for correlation coefficients were either performed as described in Miller and Miller [2005] or with Microsoft Excel[®]. Orthogonal Distance Regression, used for fitting data with statistical uncertainties in both the dependent and independent variable, was performed on IGOR Pro[®] software and multi-variate ANOVA was carried out with Minitab[®] software.

All statistical significance tests, unless stated otherwise, were performed at a significance level of $P = 0.05$.

2.4.2 Calibration and data analysis

Calibration curves were constructed each week with a series of freshly-prepared standards. Concentrations of methyl halides in the gases used for dilution of primary standards varied with time and hence the exact composition of the final calibration standards changed over time as well; however the nominal concentrations of CH₃Br and CH₃Cl in the final standards did not (Table 2.1b).

2.4.2.1 Standard make-up

A 5 L Tedlar bag was filled with 50 mL each of the two certified primary standards, 500±10 ppbV CH₃Br in N₂ (Air Products Inc., Allentown, PA, USA) and 15.8±0.47 ppmV CH₃Cl in N₂ (Air Liquide, Paris, France), and then made up to exactly 5 L with either lab air, zero air or nitrogen. This secondary standard was then further diluted in 5 L Tedlar bags to make up the final calibration standards (Table 2.1a). Before modification of the ECD, only CH₃Br standards were made.

An important issue was the improvement of the blank samples. At the start of the project the individual calibration standards were made up by diluting the respective primary standards

Table 2.1: Standard concentrations as were made weekly and changes made to the calibration mixture over time. The changes mainly reflect the beginning of regular CH₃Cl measurements and the switch-over to absolute zero blanks for absolute concentration measurements.

(a) Calibration standards		(b) Dates of changes made to the calibration make-up regime	
CH ₃ Br / pptV	CH ₃ Cl / pptV	Date	Standard make-up
0	0	08.01.2007 to 19.11.2007	CH ₃ Br in lab air
10	316	07.01.2008 to 28.04.2008	CH ₃ Br and CH ₃ Cl in lab air
25	790	05.05.2008 to 03.09.2008	CH ₃ Br and CH ₃ Cl in charcoal and Tenax filtered Zero Grade air
50	1 580	23.09.2008 to 28.08.2009	CH ₃ Br and CH ₃ Cl in Research Grade N ₂
100	3 160		
250	7 900		
500	15 800		

in lab air and the calibration blank was lab air alone. This method was adequate to measure relative concentration differences and had several advantages. Besides being simple and cost effective, it also meant that the matrix in the calibration standards was very similar to that of the samples to be analysed. On the other hand it made it impossible to determine absolute concentrations and the inherent concentration changes in the blanks were a source of statistical variation that impacted on the precision of the calibration standards and therefore the calibration curves. This in turn was detrimental for the precise determination of methyl halide fluxes and raised the limit of detection (LOD) as well. In order to improve on this, the gas used to dilute the calibration standards was first changed to Zero Grade air which had been filtered through a bed of activated charcoal and Tenax-TA 60/80 at a temperature of -78°C . Although this method significantly minimised the blank signal for both methyl halides, it was deemed impractical for routine applications. Instead, commercially available Research Grade N₂ was used. The improvement which had resulted from this change did not last until the end of the project due to impurities in the N₂ make-up gas for the ECD (Figure 2.10).

2.4.2.2 Linear regression

Assuming that the detector response is linear over the range of the calibration curve—which was checked each time—then linear regression can be used to quantify the calibration curve [Miller and Miller, 2005].

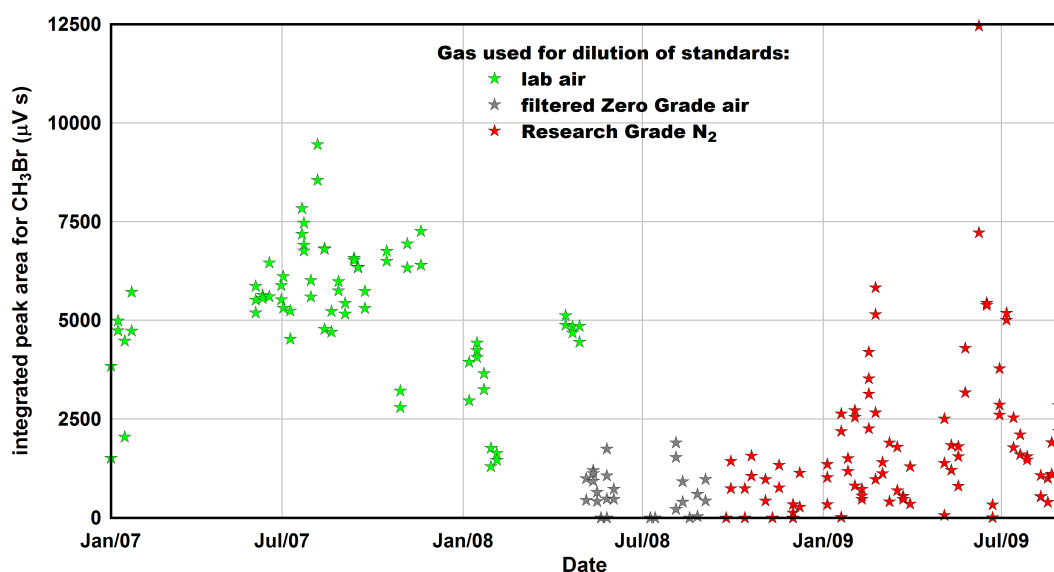


Figure 2.10: Blank signals for CH₃Br during 2½ years of the PhD project. The changes in detector response after January 2009 were due to impurities in the N₂ make-up gas stream of the GC-ECD system.

2.4.2.3 Calculation of fluxes from CH₃X volume mixing ratio determination

Once the methyl halide gas mixing ratios for both the enclosure and the background/blank samples are analysed the corresponding flux can be calculated. Although the flux calculations for the different enclosure types differ in some ways, the underlying principles are the same.

The general formula for calculating a methyl halide flux F_{general} from a static enclosure is:

$$F_{\text{general}} = \frac{\Delta c \times n \times M_R}{t \times X} \quad (2.4.1)$$

where:

Δc = mixing ratio difference between enclosure sample and background/blank sample (= pptV $\times 10^{-12}$)

n = amount of an ideal gas inside enclosure (mol)

M_R = molar mass of either CH₃Br or CH₃Cl taken from literature (g mol⁻¹)

t = duration of enclosure experiment (min)

X varies between the different enclosure types and will be discussed below

Most of the values going into Equation (2.4.1) are easily obtained and only n needs to be resolved. By applying the Ideal Gas Law n can be indirectly measured through the atmospheric pressure p (Pa), the chamber volume V (m³), the molar gas constant R

(8.31451 J K⁻¹ mol⁻¹) and the air temperature T ($x+273.2$ °C).

$$nRT = pV \quad (2.4.2)$$

By rearrangement of Equation (2.4.2), and substitution into Equation (2.4.1), Equation (2.4.3) which includes only known values is derived:

$$F_{\text{general}} = \frac{\Delta c \times \frac{pV}{R \times T} \times M_R}{\frac{t}{60} \times X} \quad (2.4.3)$$

For salt marsh measurements X represents area A :

$$X = A \quad A = \text{area of internal chamber footprint (m}^2\text{)}$$

$$F_{\text{salt marsh}} = \text{ng m}^{-2} \text{ h}^{-1}$$

For greenhouse measurements X represents total dry plant mass, m :

$$X = m \quad m = \text{total dry plant mass (g)}$$

$$F_{\text{greenhouse}} = \text{ng g}^{-1} \text{ h}^{-1}$$

For branch measurements X represents total dry mass of leaves enclosed by the branch chamber:

$$X = m_{\text{foliage}} = n_{\text{leaves}} \times \bar{m}_{\text{dried leaves}} \quad (2.4.4)$$

$$n_{\text{leaves}} = \text{number of leaves enclosed by branch chamber}$$

$$\bar{m}_{\text{dried leaves}} = \text{average dry mass of individual leaves from branch (g)}$$

$$F_{\text{branch}} = \text{ng g}^{-1} \text{ h}^{-1}$$

For leaf litter measurements X represents total dry mass of the leaf litter in the bucket and therefore:

$$X = m_{\text{litter}}$$

$$m_{\text{litter}} = \text{total mass of oven-dried leaf litter (g)}$$

$$F_{\text{litter}} = \text{ng g}^{-1} \text{ h}^{-1}$$

Atmospheric pressure was not normally measured but assumed to be equal or very near the standard pressure of 101.325 kPa. Only the greenhouse experiments were conducted in an artificial low pressure environment and therefore the air pressure had to be measured on each occasion and was used for the calculations instead. For flux measurements of leaf and

needle litter in temperate forests the volume occupied by the litter inside the enclosure was calculated from density measurements and the mass of dry litter and subtracted from the chamber volume. For all other enclosures, the volume of the enclosed object of study was taken as zero.

2.4.3 Error calculations

In order to gain a reasonable estimate of uncertainty for each flux determination the different sources of statistical error must be identified and quantified.

2.4.3.1 Error sources for methyl halide fluxes

The sources of statistical uncertainty impacting on the precision of the final flux value F_{general} Equation (2.4.1) were assumed as follows:

- Δc was often the largest single error source and is discussed in detail below
- p was assumed to have no uncertainty associated with it
- V was assigned different uncertainty values according to the measurement type conducted
 - For salt marsh measurements the uncertainty in chamber volume s_V was estimated as $1.9 \times 10^{-3} \text{ m}^3$.
 - For greenhouse enclosures s_V was estimated as $1.0 \times 10^{-3} \text{ m}^3$.
 - For branch enclosures in Borneo s_V was estimated to be $1.5 \times 10^{-3} \text{ m}^3$ and $2.5 \times 10^{-3} \text{ m}^3$ for small and large chambers, respectively.
 - For leaf litter enclosures in Borneo s_V was estimated at $1.0 \times 10^{-3} \text{ m}^3$.
 - For leaf litter enclosures in Scotland s_V was deemed negligible.*
- T was assumed to have an uncertainty s_T of 3 K for all measurements other than the greenhouse study where it was assumed to be 1 K

*The main source of error for s_V was the volume taken up by the leaves themselves. However, for temperate forest measurements the leaf litter volume was well known and the uncertainty in this measure very small.

- t was assigned different uncertainty values (s_t) again depending on the enclosure type and enclosure time
 - For salt marsh enclosures that lasted typically 10 min, s_t was assumed to be 20 s (0.0056 h).
 - For greenhouse enclosures (2.5 min long) s_t was assumed to be 10 s (0.0028 h).
 - The uncertainty for branch enclosures (20 min long) was taken as 30 s (0.0083 h).
 - Tropical leaf litter enclosures were all 24 h in duration and had an associated uncertainty of 10 min (0.17 h).
 - Temperate leaf litter enclosures lasted for either 10 min, 1 h, 6 h or 24 h with associated s_t values of 0.0056, 0.02, 0.25 and 0.25 h, respectively.
- For greenhouse, leaf litter and branch enclosures the mass of dried plant material m was another source of statistical uncertainty. For all leaf litter enclosures, and for the greenhouse enclosures, measurement uncertainties of 15 g and 1.5 g respectively were assumed. However, since the uncertainty s_m for branch measurements was likely to be more variable and more important it had to be calculated separately for each enclosed branch individually from the standard error of the mean of the average leaf mass (Equation (2.4.8)).

Any other sources of error not mentioned here were dismissed as being insignificant contributors to the overall uncertainty of the calculations.

The two principle, and more complex, sources of uncertainty, the before/after- enclosure concentration difference Δc , and the total dry mass, m , for branch enclosures are discussed next in more detail.

2.4.3.2 Statistical uncertainty of instrumental methyl halide analysis

The uncertainty value $s_{\Delta c}$ of the concentration difference Δc between the enclosure sample and the concurrent background/blank sample is itself derived from the statistical uncertainties of the latter two. Assuming that any statistical error for both values is solely due to the GC measurements (i.e. it is assumed that the sample concentrations are not subject to statistical variation from sample collection or storage) then a straightforward formula can be applied. As described above individual methyl halide concentrations are derived from the

interpolation of a calibration curve. The formula for the error in an interpolated value is:

$$s_{x_0} = \frac{s_{y/x}}{b} \sqrt{\frac{1}{m_{\text{measurement}}} + \frac{1}{n_{\text{standards}}} + \frac{(y_0 - \bar{y})^2}{b^2 \sum_i (x_i - \bar{x})^2}} \quad (2.4.5)$$

where s_{x_0} is the statistical uncertainty for an individual interpolated concentration value x_0 with its associated detector response y_0 . b is the slope of the calibration curve, $m_{\text{measurement}}$ is the number of repeat measurements used to determine the sample concentration, $n_{\text{standards}}$ is the number of standards measured to construct the calibration curve and x_i is the concentration of an individual calibration standard, \bar{x} and \bar{y} are the mean standard concentration and the mean detector response respectively. $s_{y/x}$ is a measure of the errors in the y -direction in the calibration curve and is defined as:

$$s_{y/x} = \sqrt{\frac{\sum_i (y_i - \hat{y}_i)^2}{n_{\text{standards}} - 2}} \quad (2.4.6)$$

with \hat{y}_i being the y -values calculated for the individual x -values from the calibration curve.

The first part of Equation (2.4.5) incorporates the size of the y -residuals between the fitted and actual detector signals from the calibration curve to quantify the variability of detector response. The first two terms under the square root account for a decreasing statistical uncertainty with increasing numbers of calibration points and sample replications. The last term under the square root relates to how near the actual y -value of an individual sample is to the centre of the calibration curve; the statistical error grows the further a y -value is from the value of \bar{y} .

Once both the statistical concentration uncertainties of a sample s_{sample} and its corresponding background/blank sample $s_{\text{background}}$ have been calculated the overall uncertainty $s_{\Delta c}$ for the concentration difference is calculated as:

$$s_{\Delta c} = \sqrt{s_{\text{sample}}^2 + s_{\text{background}}^2} \quad (2.4.7)$$

2.4.3.3 Statistical uncertainty of total leaf material mass

To calculate a reasonable measure of uncertainty of the mass of leaf material on a branch, it has to be recalled that the latter is calculated by multiplying the average mass of a number of leaves taken from this branch with the number of leaves on the branch (Equation (2.4.4)). Assuming that the leaves were counted accurately only the average mass of the leaves remains

as a source of uncertainty. The best statistical measure is the standard error of the mean s_{foliage} which takes account of both the variability of the average leaf weight $\bar{m}_{\text{dried leaves}}$ and of the number $n_{\text{leaves weighed}}$ of leaf samples used to derive this average value:

$$s_{\text{foliage}} = \frac{\sqrt{\sum_i (m_{i, \text{leaf}} - \bar{m}_{\text{dried leaves}})^2 / (n_{\text{leaves weighed}} - 1)}}{\sqrt{n_{\text{leaves weighed}}}} \quad (2.4.8)$$

with $m_{i, \text{leaf}}$ being the mass of each individual leaf that was weighed.

2.4.3.4 Final error propagation calculations

Finally the overall uncertainties for a flux are calculated as:

$$\begin{aligned} s_{F_{\text{salt marsh}}} &= F_{\text{salt marsh}} \times \sqrt{\left(\frac{s_{\Delta c}}{\Delta c}\right)^2 + \left(\frac{s_V}{V}\right)^2 + \left(\frac{s_T}{T}\right)^2 + \left(\frac{s_t}{t}\right)^2} \\ s_{F_{\text{greenhouse}}} &= F_{\text{greenhouse}} \times \sqrt{\left(\frac{s_{\Delta c}}{\Delta c}\right)^2 + \left(\frac{s_V}{V}\right)^2 + \left(\frac{s_T}{T}\right)^2 + \left(\frac{s_t}{t}\right)^2 + \left(\frac{s_m}{m}\right)^2} \\ s_{F_{\text{branch}}} &= F_{\text{branch}} \times \sqrt{\left(\frac{s_{\Delta c}}{\Delta c}\right)^2 + \left(\frac{s_V}{V}\right)^2 + \left(\frac{s_T}{T}\right)^2 + \left(\frac{s_t}{t}\right)^2 + \left(\frac{s_{\text{foliage}}}{m_{\text{foliage}}}\right)^2} \\ s_{F_{\text{litter, tropical}}} &= F_{\text{litter}} \times \sqrt{\left(\frac{s_{\Delta c}}{\Delta c}\right)^2 + \left(\frac{s_V}{V}\right)^2 + \left(\frac{s_T}{T}\right)^2 + \left(\frac{s_t}{t}\right)^2 + \left(\frac{s_{\text{litter}}}{m_{\text{litter}}}\right)^2} \\ s_{F_{\text{litter, temperate}}} &= F_{\text{litter}} \times \sqrt{\left(\frac{s_{\Delta c}}{\Delta c}\right)^2 + \left(\frac{s_T}{T}\right)^2 + \left(\frac{s_t}{t}\right)^2 + \left(\frac{s_{\text{litter}}}{m_{\text{litter}}}\right)^2} \end{aligned}$$

2.4.4 Limit of detection

To determine whether or not a net flux was significant it had to be affirmed that there was a significant enough difference between the mixing ratio of a sample and its concurrent background/blank sample. This means that the determination of a significant flux was in fact made solely on the basis of the GC analysis and its associated statistical errors (Equation (2.4.5)). Assuming the two concentrations x_{sample} and $x_{\text{background}}$ are truly different then even taking into account that both have a statistical uncertainty s_{sample} and $s_{\text{background}}$ respectively they have to fulfil the following requirement:

$$(x_{\text{sample}} \pm s_{\text{sample}}) \neq (x_{\text{background}} \pm s_{\text{background}}) \quad (2.4.9)$$

If both concentrations are very similar then their associated uncertainties also become similar since their magnitude largely depends on the position of the y -values relative to the centre of the calibration curve. Equation (2.4.9) can thus be transformed into:

$$\begin{aligned}(x_{\text{sample}} \pm s_{\text{background}}) &\neq (x_{\text{background}} \pm s_{\text{background}}) \\ x_{\text{sample}} &\neq (x_{\text{background}} \pm 2s_{\text{background}})\end{aligned}\tag{2.4.10}$$

Thus any flux measurement that did not fulfil Equation (2.4.10) was assumed to be zero and for all further purposes treated as such. This included any further statistical treatment of results such as average seasonal fluxes, average diurnal fluxes, scale-up etc. It has to be made absolutely clear that the significance of a flux was solely decided on the basis that there was a significant difference in mixing ratio before and after an enclosure, since this was taken as proof that methyl halides have been either taken up or produced. No other source of statistical uncertainty was taken into consideration. Therefore any non-zero flux presented in this report was treated as significant even if its associated overall error would bring its absolute value over the zero line. Here the uncertainty value only represents an uncertainty in the strength of a flux but not its statistical significance.

2.4.5 Stability study

Several stability studies were carried out to ensure that gas samples did not deteriorate appreciably during storage and to determine maximum storage times.

The basic concept was to monitor the concentration of methyl halide standards in the various sample bag types over time. The most thorough study was carried out during January and February 2008 on 18 1 L Tedlar bags. Half of these were filled with a mixture of 10 pptV CH₃Br and 316 pptV CH₃Cl, the other half with a mixture of 250 pptV CH₃Br and 7 900 pptV CH₃Cl. Three bags each were held for 31 d at either room temperature ($\sim 20^\circ\text{C}$), 30°C or 40°C . Samples were taken on days 1, 3, 6, 10, 17, 25 and 31. Concentrations were determined by comparison to nominally equal standards that were made up and run during the weekly calibration.

Smaller stability studies were carried out on both FEP and Cali-5-Bond bags to determine their performance in comparison to the Tedlar bags. These studies were primarily aimed to help the decision on the possible purchase of these bag types for the Borneo campaign and were therefore much smaller in scale. Both studies were performed on 4 bags each, filled with a 500 pptV CH₃Br standard; two bags each were stored at room temperature and 40°C respectively. Concentration measurements were run together with weekly calibrations

and CH_3Br concentrations were determined by applying both slope and intercept of the calibration curve to the raw peak data.

As can be seen in Figure 2.11 there was no appreciable difference in the concentration decline of CH_3Br between the three different bag types for a particular temperature regime. However

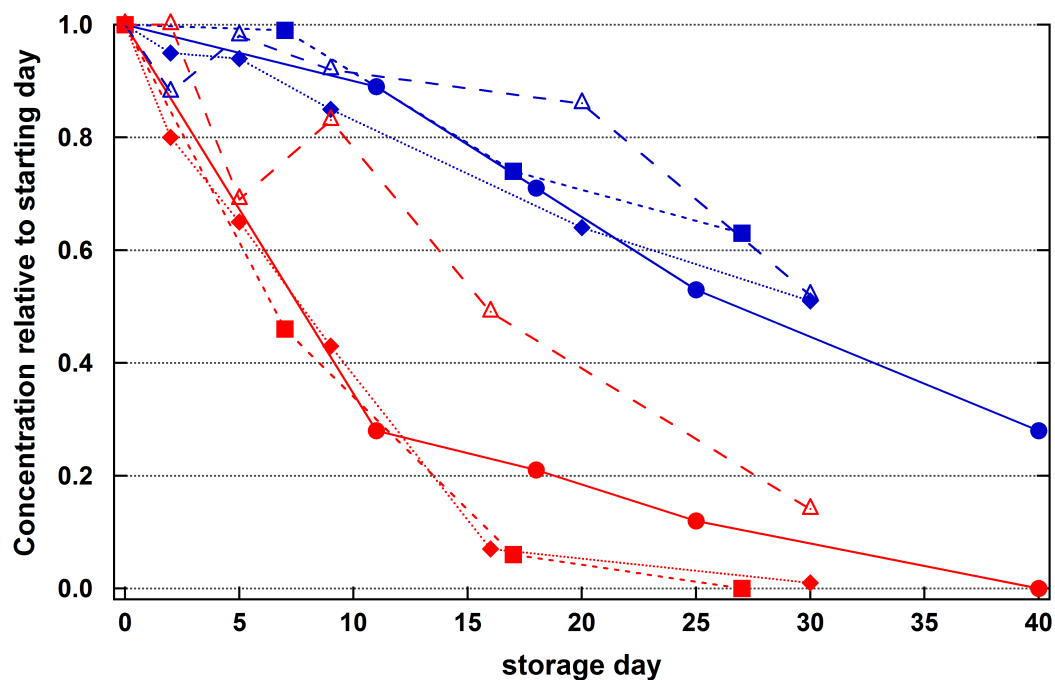


Figure 2.11: Stability study of CH_3Br and CH_3Cl in FEP-, Cali-5-Bond- and Tedlar- bags: CH_3Br in FEP bags (—●—), CH_3Br in Cali-Bond bags (—■—), CH_3Br in Tedlar bags (—◆—) and CH_3Cl in Tedlar bags (—△—) at ambient temperature, CH_3Br in FEP bags (—●—), CH_3Br in Cali-5-Bond bags (—■—), CH_3Br in Tedlar bags (—◆—), CH_3Cl in Tedlar bags (—△—) at 40 °C respectively.

there was an appreciable difference between the gas samples being stored at ambient temperature and 40 °C. The difference in the progression of the curves for CH_3Cl and CH_3Br in Tedlar bags at ambient temperatures was negligible. However at 40 °C concentration decline for CH_3Cl was less pronounced than for CH_3Br . The reasons for the concentration decline can only be speculated. However it is likely that part of the methyl halides reacts with the oxygen and water vapour in the gas phase leading to oxidation and hydrolysis reactions, which would be expected to speed up at higher temperatures. Also CH_3Cl is expected to be less likely to undergo such a reaction compared to CH_3Br . Another possible sink in the bags was the migration of methyl halides into the bag walls, a process expected to shift towards a thermodynamic balance. This is supported by the observation that sample bags filled with very high CH_3Cl concentrations were found to contain high levels of CH_3Cl after they had been flushed with research grade nitrogen several times. This problem caused the loss of several samples and was only remediated through long term storage of the contaminated

bags and regular replacement of the research grade nitrogen contained within them. Again this process is likely to speed up with higher temperatures.

Gas samples were usually analysed within one week, however some gas samples from Borneo were stored up to two weeks between sample retrieval and final analysis. Given that gas samples were stored at ambient temperatures and in the dark it seems reasonable to suggest that a maximum concentration loss of no more 10 % and 20 % would have occurred for samples taken in Scotland and Borneo, respectively.

Chapter 3

Long-term flux measurements in temperate salt marshes

3.1 Introduction

Of all terrestrial ecosystems, salt marshes are the most likely to produce both CH_3Br and CH_3Cl in large quantities. They contain naturally high amounts of readily available bromine and chlorine in both soil and plant material and are highly productive ecosystems [Rhew et al., 2002]. For these reasons salt marshes could account for a considerable part of the missing global sources of both gases, despite the relatively small surface area ($< 0.1\%$ of total global surface area [Butler, 2000]) that they occupy.

A number of studies of methyl halide fluxes in salt marshes have been conducted throughout the world with contrasting results. Rhew and co-workers [Rhew et al., 2000, 2002; Bill et al., 2002] studied fluxes of CH_3Br and CH_3Cl in two salt marshes in Southern California, subject to Mediterranean climate. However, it is not clear how the reported individual measurements in these studies were scaled up to estimate global emissions. Rhew et al. [2000, 2002]; Bill et al. [2002] used opaque static chambers of 1 m^2 area and 850 L volume and identified vegetation type, plant biomass, season and time of day as the main factors of variations in the flux rates. Due to the use of opaque chambers, flux variations over the length of day and season were more likely to be associated with air temperature rather than incident sunlight although emission patterns followed both. Fluxes during the growing season were up to 10 times higher than fluxes during the non-growing season and diurnal fluxes varied by a factor of 4 for CH_3Br and 1.4 for CH_3Cl . Rhew et al. [2002] identified salt marsh soil as a small net source of both methyl halides and reaffirmed that higher plants were the main source. CH_3Br and CH_3Cl fluxes in this study were correlated both in seasonal and diurnal measurements, suggesting that the same underlying production/consumption processes were responsible for both gases. However, they also observed a diurnal variation in the $\text{CH}_3\text{Cl}/\text{CH}_3\text{Br}$ mass

ratio, being ~ 5 during the day and ~ 20 during the night time. The $^{13}\text{C}/^{12}\text{C}$ isotope ratio during night (-70‰ for both) and daytimes (-10‰ for CH_3Br and -40‰ for CH_3Cl) were different which suggests that at least two competing production/consumption processes were occurring at different strengths over the length of a day. The main difficulty in the studies of Rhew and co-workers was that fluxes were measured in darkness. It is therefore not clear how fluxes might have correlated with incident sunlight, if at all. They estimated that approximately 7 % of global CH_3Br and 5 % of global CH_3Cl (equivalent to average fluxes of $4\,210\text{ ng m}^{-2}\text{ h}^{-1}$ and $51\,100\text{ ng m}^{-2}\text{ h}^{-1}$, respectively, calculated from data in Rhew et al. [2000]) could potentially be produced in this environment.

A study by Manley et al. [2006], also located in Southern California and describing the same plant species as Rhew et al., came to similar conclusions. Sampling during daylight hours at fortnightly intervals on mono-specific stands and bare soil/mud for 1–2 yr with translucent chambers, Manley et al. identified changes in monthly average solar radiation and physiological changes such as flowering as the main drivers for flux variations of the two gases. Emission estimates normalised to tissue biomass revealed moderate to strong correlation ($R > 0.7$) between CH_3Br and CH_3Cl emissions for each species (except *Salicornia virginica*) in this study. Average fluxes of CH_3Br and CH_3Cl between different plant species varied by up to two orders of magnitude whereas inter-species differences of average $\text{CH}_3\text{Cl}/\text{CH}_3\text{Br}$ mass ratios were small. Soils were identified as weak methyl halide emitters for most of the year, except on some occasions in winter. Scaling up was conducted in two different ways: by either scaling fluxes from the main species and bare soil/mud normalized to their respective land cover at the study site or by scaling fluxes from the different species alone, excluding non-vegetated areas. This resulted in average fluxes of $2\,400\text{ ng m}^{-2}\text{ h}^{-1}$ and $14\,800\text{ ng m}^{-2}\text{ h}^{-1}$ including soils and $7\,300\text{ ng m}^{-2}\text{ h}^{-1}$ and $46\,800\text{ ng m}^{-2}\text{ h}^{-1}$ excluding soils for CH_3Br and CH_3Cl respectively. The latter estimate is similar to the result calculated from Rhew et al. [2000] for CH_3Cl but higher than the CH_3Br fluxes reported there. Diurnal variations were not considered in the up-scaling since they had not been part of the study.

In contrast to the previous two studies, Wang et al. [2006] reported strong consumption of CH_3Cl at a salt marsh in Eastern China. Net consumption was shown to be a product of strong uptake reactions in the soil and weak production by vegetation. This was supported by the fact that positive fluxes were observed when soil was either inundated or frozen. Wang et al. also reported that the CH_3Cl production was positively correlated with sunlight levels but negatively correlated with soil temperature, soil organic matter (SOM) content and CH_3Cl concentration in ambient air, again suggesting processes of production by plants and microbial uptake in soils. One explanation for the observed strong CH_3Cl uptake may be that the CH_3Cl concentration in the background air was over 58 ppbV which is 100 times greater than the usual background concentration. Another reason could be that the vegetation

differs from the other study sites. Wang et al. also assumed that the high CH_3Cl in ambient air led to a higher concentration of microbes living on CH_3Cl as their sole energy source.

A diurnal study of coastal peatlands near Mace Head, Ireland, by Dimmer et al. [2001] during three days in September 1998 included flux measurements from one salt marsh site using a translucent chamber. A strong diurnal cycle for methyl halide emissions was found. Highest fluxes were measured at 14:00 and lowest fluxes were observed between 18:00 and 07:15, with a daytime:night-time ratio of approximately 4:1 for CH_3Br and 5:1 for CH_3Cl . Dimmer et al. related this finding to sunlight levels rather than temperature, as the latter did not change significantly over the measurement period. The average production rates of CH_3Br and CH_3Cl were reported as $320 \text{ ng m}^{-2} \text{ h}^{-1}$, ranging from 91 to $502 \text{ ng m}^{-2} \text{ h}^{-1}$ for CH_3Br , and $377 \text{ ng m}^{-2} \text{ h}^{-1}$, ranging from 23 to $548 \text{ ng m}^{-2} \text{ h}^{-1}$ for CH_3Cl . The $\text{CH}_3\text{Cl}/\text{CH}_3\text{Br}$ mass ratios were ~ 1.2 ; low compared to the previously discussed studies. Emissions of both gases were strongly correlated ($R^2 = 0.91$) which was attributed to diffusion control of fluxes. Dimmer et al. also assessed the influence of enclosure time reporting that after 15 min the flux rate ceased to be linear and began to fall. This is important for the design of flux chambers techniques where non-linear behaviour of gas fluxes should be avoided where possible.

Cox et al. [2004] performed monthly daytime measurements at Robins Crossing, a Tasmanian salt marsh site, for one year, using a transparent dynamic chamber. Again the emissions of CH_3Br and CH_3Cl were reported to be strongly correlated and showed a seasonal response with higher fluxes during the summer time. Cox et al. attributed this to the influence of the deciduous vegetation at the salt marsh site. Mean fluxes were $190 \text{ ng m}^{-2} \text{ h}^{-1}$, ranging from 27 to $470 \text{ ng m}^{-2} \text{ h}^{-1}$, and $300 \text{ ng m}^{-2} \text{ h}^{-1}$, ranging from -34 to $760 \text{ ng m}^{-2} \text{ h}^{-1}$, for CH_3Br and CH_3Cl , respectively. Again $\text{CH}_3\text{Cl}/\text{CH}_3\text{Br}$ mass ratios were considerably lower (2.0 ± 0.2) than those reported for Californian salt marshes [Rhew et al., 2000; Manley et al., 2006].

Drewer et al. [2006], from this research group, measured CH_3Br fluxes at Heckie's Hole, a salt marsh near Dunbar, Scotland for over one year, including diurnal studies in different seasons. Although measurements were conducted with partially transparent chambers they concluded that sunlight rather than air temperature was the main controlling factor for diurnal variation and could not reconcile their findings with those of Rhew et al.. Drewer et al. reported average salt marsh fluxes of $350 \text{ ng m}^{-2} \text{ h}^{-1}$ and therefore a factor of 10 lower than Rhew et al.'s results. Further experiments on soil cores with intact vegetation cover, collected from the salt marsh [Drewer et al., 2006], showed a clear rise in concentrations after addition of NaBr solution, which increased soil Br^- concentrations about 75 fold of ambient. A similar experiment with sea water addition did not show significant enhancement in emissions and raising soil moisture resulted in increased emissions on some occasions. However in all of these experiments CH_3Br emissions markedly dropped after removal of the vegetation at the

end of each experiment. An experiment testing the influence of enclosure time on CH_3Br flux rates concluded that emissions decreased with an increase in enclosure time, similar to Dimmer et al.'s findings, again stressing the need of careful experimental design.

All the above studies came to the conclusion that vegetation in salt marshes acted as the main source of methyl halides. They also concluded that methyl halide production by plants was proportional to halide concentration in the soil, and that it was highly dependent on species, season and above ground biomass of plants. Most studies also found that soils are methyl halide sources of varying strength and all except Rhew et al. identified sunlight level as the most likely driver for diurnal emission patterns. Fluxes differed significantly both within and between the measurement sites, highlighting the need for a greater number of measurements at more sites to build up a better global picture of methyl halide fluxes in salt marshes. Furthermore it is necessary to pinpoint what is driving methyl halide production from plants and to assess the strength of the link between different species, biomass and methyl halide production. This is especially important for modelling studies of global methyl halide fluxes where currently short, spatially restricted datasets are used to arrive at global estimates.

The objectives of the work described in this chapter were therefore to:

1. Quantify methyl halide fluxes in temperate salt marshes.
2. Quantify variations in methyl halide fluxes between different salt marsh sites.
3. Identify possible drivers of methyl halide fluxes from salt marshes.

3.2 Locations and Descriptions of salt marsh study sites

The two study sites, Heckie's Hole and Hollands Farm located on the east and west coast of Scotland, respectively, were chosen for their contrasting geography and ease of access.

3.2.1 Heckie's Hole

Heckie's Hole near the hamlet of Tynningham is located in the estuary of the River Tyne as it flows into the North Sea (Figure 3.1) and is part of the John Muir Country Park. As illustrated in Figure 3.2 Heckie's Hole is enclosed on three sides by agricultural and forested land and is connected to the open sea by an indirect route. The site comprises the salt marsh (approximately $\frac{1}{3}$ of area) which sharply rises from the mudflats (approximately $\frac{2}{3}$ of area).

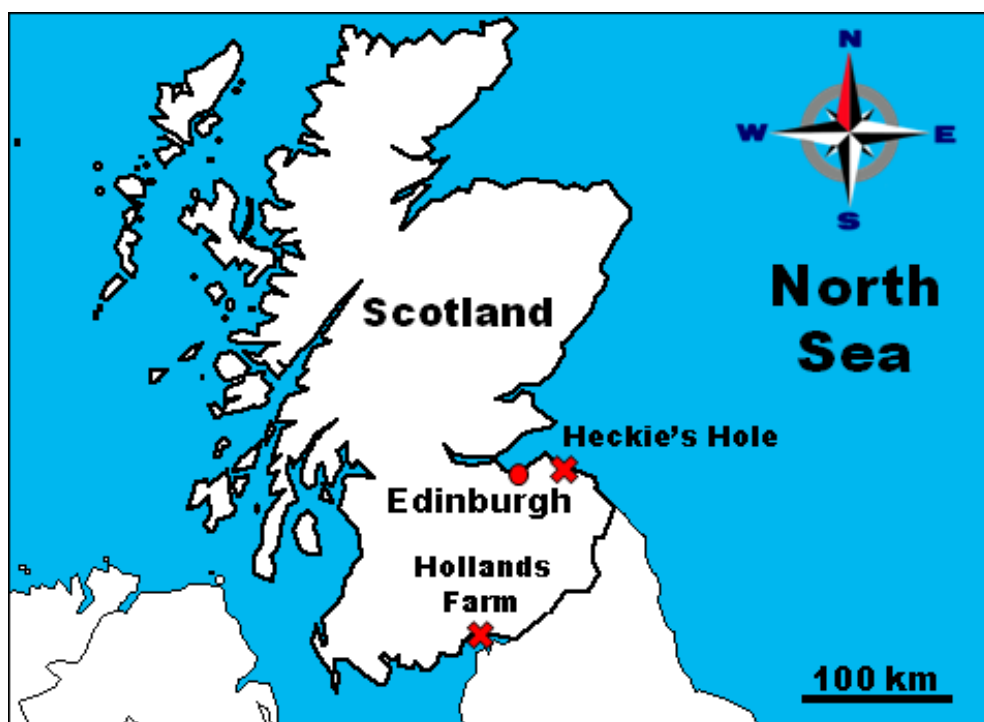


Figure 3.1: Map of Scotland showing the approximate locations of the two salt marsh sites.

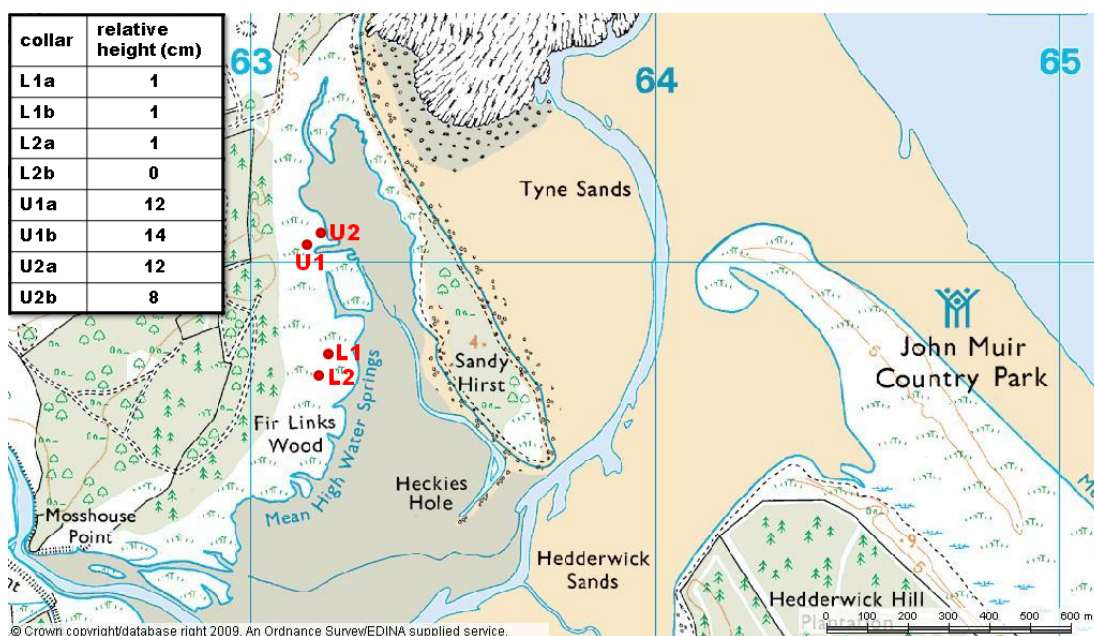


Figure 3.2: Map of Heckie's Hole showing the positions of the four collar pairs. The indirect access to the open sea to the east prevents direct wave action on the salt marsh. The inset table lists the relative height of individual collars in the marsh as measured in this study; the zero reference point was the lowest point measured.

The salt marsh is approximately one metre higher than the mudflats and forms a plateau sloping gently upwards towards the mainland.

The salt marsh contains a large number of deep tidal creeks (approximately 0.5 m lower) which are regularly flooded during high tides (Figure 3.3). The rest of the salt marsh is subject to flooding every fortnight from spring tides [Drewer, 2010]. Rather than experiencing accretion/erosion at its boundary to the mudflats the salt marsh is accreting and eroding mainly through the creeks.



Figure 3.3: Aerial photo of Heckie's Hole taken in June 2008 showing the extensive channel system through which the salt marsh is growing and eroding. The pink colour on the right side of the salt marsh is the *Armeria maritima* flowers in bloom. Courtesy of East Lothian Council.

The only other topographical feature of the salt marsh is a number of unvegetated ponds, several metres wide and 10–20 cm below the rest of the marsh, that are filled with water most of the year. These ponds are cut off from the channel system and are probably the result of the collapse and infilling of old channels. Most of the salt marsh is long established i.e. not vertically accreting any more; and the vegetation at most parts of Heckie's Hole is very homogeneous and there is no strong zonation.

Two pairs of collars (Figure 3.4) were placed in the 'lower' marsh i.e. the area near the mudflats, the first pair L1a and L1b being some 50 m north of the second pair L2a and L2b (Figure 3.2). The two collar pairs representing the 'upper' marsh, i.e. towards the mainland, were collar pairs U1a and U1b, and U2a and U2b.



(a) Collar L1a, photo taken on the 12/08/08



(b) Collar L1b, photo taken on the 12/08/08



(c) Collar L2a, photo taken on the 12/08/08



(d) Collar L2b, photo taken on the 12/08/08



(e) Collar U1a, photo taken on the 12/08/08



(f) Collar U1b, photo taken on the 12/08/08

Figure 3.4: Photos of collars at Heckie's Hole.



(g) Collar U2a, photo taken on the 12/08/08



(h) Collar U2b, photo taken on the 12/08/08

Figure 3.4: Photos of collars at Heckie's Hole.

3.2.2 Hollands Farm

Hollands Farm is located 8 km south of Dumfries (South-West Scotland) on the estuary of the River Nith as it flows into the Solway Firth (Figure 3.1). It is part of the much larger Caerlaverock Merse (590 ha) stretching from east to west along the coast for 8 km [Hansom, 2003; Warren, 2010]. The salt marsh is about 500 m wide and gradually rises from the mudflats and tidal sands which stretch up to 5 km out into the firth (Figure 3.5). In contrast to the Heckie's Hole salt marsh, there is a clear vegetation zonation. The lower marsh is the pioneer zone which is currently strongly accreting soil and is sparsely vegetated by salt marsh specific plants. The uppermost part of the marsh has a higher elevation and is static and very densely vegetated and would qualify as grassland.

The salt marsh at Hollands Farm has been in decline for many decades and has only recently started to accrete again. Remnants of the old salt marsh can be found landwards where the newly established pioneer zone abruptly rises to two terrace edges ~20 cm and then another ~40 cm onto the level of the old salt marsh. Although the salt marsh contains some tidal creeks, these do not have the same function for accretion and erosion as in Heckie's Hole but rather are remnants of an older salt marsh system. Instead, soil accumulates from tidal inundation as the marsh is low lying enough to be flooded on a more regular basis. The topography of the landscape changes with distance from the sea, first being very flat and then comprising alternating hollows and hummocks with height differences of 10–15 cm. This is followed by another short stretch of shallow rise before the terrace edges that lead to the level of the old marsh.

Overall, 11 collars were installed at Hollands Farm at any one time (Figure 3.6). A single

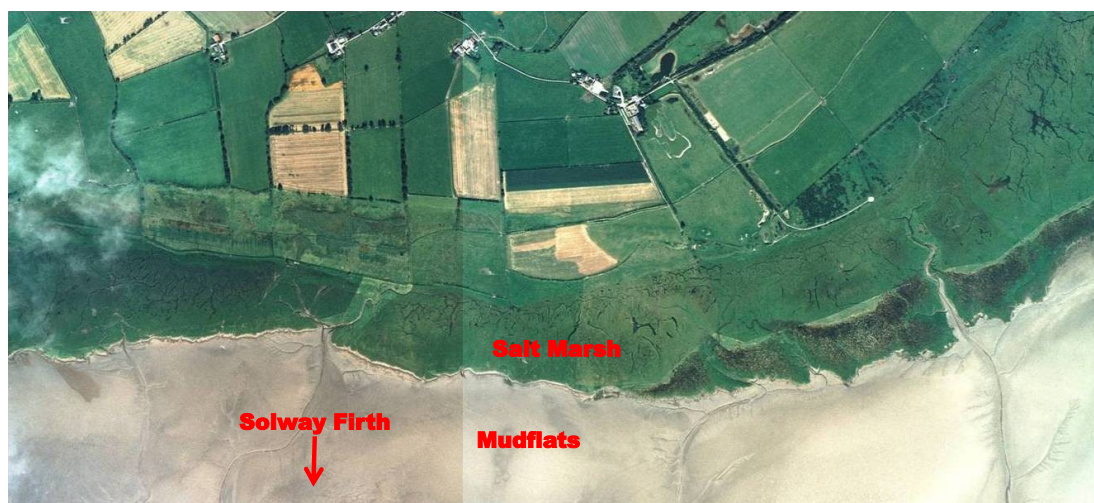


Figure 3.5: Overlay of two aerial photos of Hollands Farm taken in September 1997 showing the salt marsh and the mudflats exposed during low tide. Please note that the salt marsh has strongly accumulated new material since these photos were taken. Courtesy of Scottish Natural Heritage, East Dumfriesshire.

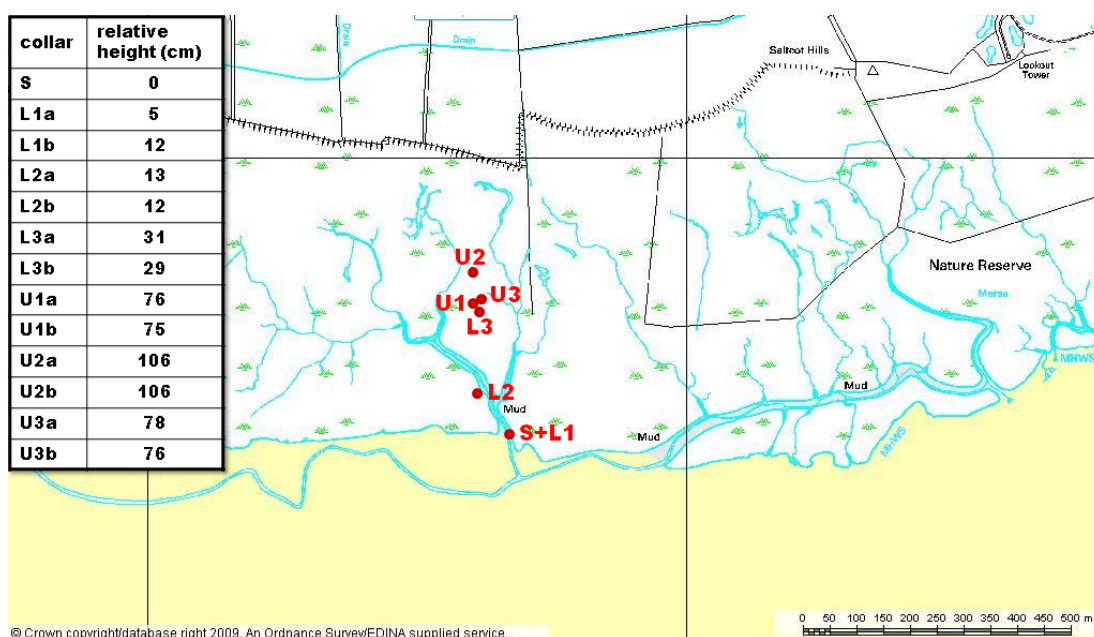


Figure 3.6: Map of Hollands Farm salt marsh. The positions of the soil collar (S) and the 6 collar pairs are shown. S and L1 are marked as one point as they were less than 10 m apart. The open access of the sea water to the salt marsh allows rapid erosion and accretion of soil. The inset table lists the relative height of individual collars in the marsh; the zero reference point was the lowest point measured.

collar (S) was placed on a bare patch of soil within the otherwise vegetated lower marsh approximately 250 m south of the upper marsh edge (Figure 3.7). Thirteen metres to the north a pair of collars (L1a and L1b) was placed on top of the aforementioned hummocks. The next pair of collars was placed approximately 90 m north-west of it in a shallow part of the marsh (collars L2a and L2b). The last pair of collars in the lower marsh (L3a and L3b) was placed 5 m south of the first terrace edge in an area that was markedly wetter than the rest of the marsh. On the first terrace, which at this point was no wider than 10 m, the first pair of collars on the upper marsh (U1a and U1b) was installed on a patch of low grasses, a second pair (U3a and U3b) only 13 m to the east of the former was placed over some taller grasses. The last pair of collars (U2a and U2b) was placed 55 m north of the second edge, in an area that is used for cattle grazing. Due to a shortage of collars the collar pair at U2 was removed in May 2008 and then placed at position U3 in the previously described position. Therefore flux measurements at position U2 were performed between 6th June 2007 to 2nd May 2008 and flux measurements at position U3 started on the 8th May 2008 until the end of the field campaign on the 21st July 2009.

3.2.3 Relative height measurements

To gain a better understanding of the influence of topography on vegetation, soil condition and possibly methyl halide fluxes, the relative heights of the tops of the different collar positions in both salt marshes were surveyed with a total station surveying system (Geodimeter 420). The lowest point measured in each salt marsh served as the reference height, above which the relative vertical levels of all other points were determined. The results of these measurements are shown in Figures 3.2 and 3.6.



(a) Collar S, photo taken on the 05/07/2007

Figure 3.7: Photos of collars from Hollands Farm.



(b) Collar L1a, photo taken on the 05/07/2007



(c) Collar L1b, photo taken on the 05/07/2007



(d) Collar L2a, photo taken on the 05/07/2007



(e) Collar L2b, photo taken on the 05/07/2007



(f) Collar L3a, photo taken on the 05/07/2007



(g) Collar L3b, photo taken on the 05/07/2007

Figure 3.7: Photos of collars from Hollands Farm.



(h) Collar U1a, photo taken on the 05/07/2007



(i) Collar U1b, photo taken on the 05/07/2007



(j) Collar U2a, photo taken on the 05/07/2007



(k) Collar U2b, photo taken on the 05/07/2007



(l) Collar U3a, photo taken on the 27/05/09



(m) Collar U3b, photo taken on the 27/05/09

Figure 3.7: Photos of collars from Hollands Farm.

3.3 Methodology

3.3.1 Site characterisation

3.3.1.1 Water table depth

To measure water table depth at each sampling location a perforated 50 cm long \times 3.4 cm outer diameter polypropylene pipe was inserted into a cylindrical hole made with an auger no further than 2 m from the collars. The pipes were covered with a lid to avoid water and soil entry during high tides. Water level below the salt marsh surface was measured with a steel tape measure on each day gas samples were taken from the flux chambers.

3.3.1.2 Soil analysis

To obtain a better understanding of differences between the two salt marsh sites, and between the different measurement positions within each site, soil cores were collected on the 3rd August 2009 at Heckie's Hole and 4th August 2009 at Hollands Farm. Samples were taken at 0–5, 5–10 and 10–15 cm depth and analysed for volumetric water content, gravimetric water content, bulk dry density, organic matter content and particle size distribution.

Field sampling Cores were taken with aluminium rings, 73 mm inside diameter and 50 mm height. At each sample location above-ground vegetation was removed using scissors. The sampling ring was hammered gently into the ground until flush and then carefully dug out with a trowel and cut off at the bottom with a knife. The soil in the ring was then extracted and stored in a pre-weighed tin container sealed within an air-tight plastic bag. The ring was then hammered into the ground exactly at the same position where the previous sample was taken. This procedure was repeated once more. At Heckie's Hole one set of cores was taken between each pair of collars. At Hollands Farm one set of cores was taken to represent collars S, L1a and L1b, and one set for collar pairs U1 and U3 since in both cases the collars were close together in a rather uniform area. The remaining collar pairs at Hollands Farm were represented by one set of cores each.

Determination of water content, dry bulk density (DBD) and soil organic matter (SOM) content Sample analysis in the laboratory started on the same day as field collection. The tins with the samples were weighed, then a small amount of soil removed for particle

size analysis, sealed in an air-tight zipper-bag and stored in a fridge whilst the remaining soil in the tin was reweighed, and then dried in an oven at 105 °C to constant weight. The oven-dry samples were cooled for 10 min in a desiccator and then weighed. The dried soil material was ground using a pestle and mortar and passed through a 250 µm sieve. Care was taken to exclude any macroscopic plant material from the soil where possible. The ground sample powder was put in a pre-weighed tin, dried at 105 °C overnight in an oven, cooled for 10 min in a desiccator, weighed, put in a furnace for 6 h at 500 °C, re-homogenised to ensure complete combustion of all the organic material and then put back into the furnace at 500 °C for another 6 h. Finally the samples were held overnight at 105 °C to keep them dry, before being cooled in a desiccator for 10 min and reweighed.

Particle size analysis The samples from Hollands Farm were prepared for particle size analysis as follows. Approximately 0.5 g of fresh soil sample was weighed into a 50 mL beaker and 25 mL of 4 % w/v sodium hexametaphosphate was added. The mixture was then ultra-sonicated for 10 min and if necessary mechanically broken up and homogenised with a spatula. It was then wet sieved through a 500 µm sieve with deionised water and quantitatively transferred into the particle size analyser.

Samples from Heckie's Hole were too organic-rich for the standard method used to prepare Hollands Farm samples and therefore needed pretreatment. Approximately 0.6 g of fresh soil sample was weighed into a 50 mL centrifuge tube. The tube was then filled with 30 mL of Laboratory Grade 30 % H₂O₂ solution and left standing at room temperature for 3 days. Next the tubes were centrifuged for 6 min at 8500 rpm and the supernatant semi-quantitatively removed with a teat pipette. To remove any remaining H₂O₂ which could damage the analysis instrument, the tubes were heated for a few minutes in a hot water bath. Then 25 mL of 4 % w/v sodium hexametaphosphate solution was added to each tube which was then ultra-sonicated for 10 min. Finally the mixture was wet sieved through a 250 µm sieve with deionised water and quantitatively transferred into the particle size analyser.

The instrument used for particle size analysis was a Beckmann Coulter LS230 laser diffractometer. The technique employs the scattering of light, delivered from a laser, that is passed through the sampling chamber containing the particles in suspension. The scattered light is detected by a photo-detector array and the intensity of light on each detector converted into a particle size distribution plot by an internal mathematical algorithm [Mennim, retrieved 27th December 2009].

Particle size distributions were converted into clay ($\varnothing < 2 \mu\text{m}$), silt ($2 \mu\text{m} \leq \varnothing < 50 \mu\text{m}$) and sand ($50 \mu\text{m} \leq \varnothing < 2 \text{mm}$) fractions and the soil texture for each sample classified according to the United State Department of Agriculture (USDA) classification [Soil Survey Division

Staff, 1993]. A soil texture triangle displaying the sample data was constructed to USDA guidelines with DPlot® software.

3.3.2 Flux measurements

3.3.2.1 Seasonal flux measurements

The main body of the work conducted in both salt marshes was regular seasonal flux measurements. For this purpose a collar was permanently inserted into the ground at each sampling point. Each collar was made of 10–20 cm long \times 40 cm internal diameter opaque PVC pipe and a fitting flange of the same material which had an outer diameter of approximately 50 cm. The two parts were glued together and additionally fastened with four M6 stainless steel screws. Any spaces between the two parts were sealed with silicone sealant. As far as possible the collars were inserted flush to the ground to reduce any impact the collar rims could have on the enclosed space. Ground collars were installed at Heckie's Hole on the 26th May 2007 and at Hollands Farm on the 30th and 31st May 2007. The two collars of a collar pair were placed no more than 5 m apart with a 50 cm deep dip well installed halfway between the two. The two collars of a pair were meant to represent the typical vegetation of a particular part of a salt marsh but were not intended as replicates. Flux measurements were conducted between 4th June 2007 to 20th July 2009 at Heckie's Hole and 6th June 2007 to 21st July 2009 at Hollands Farm.

To start a flux measurement a 40 cm diameter chamber was placed on top of the collar and fastened with bulldog clips. Typically, sampling for seasonal flux measurements took place between 10 am and 3 pm. However this was not always the case, particularly at the beginning of the measurement campaign. Enclosure times were 10 min and the ground chambers were 21.5 cm high (except for the 6th June 2007 at Hollands Farm where 10.5 cm chambers were used as well). Concurrently to the enclosure and the automatic monitoring of chamber temperature, PAR and total solar radiation were recorded as described in Chapter 2, as well as the air temperature, soil temperature at 10 cm depth and water level in the dip well. Soil samples for moisture determination were also taken on most measurement occasions, stored in air-tight zipper-bags for transport to the laboratory and then refrigerated until analysis.

3.3.2.2 Diurnal flux measurements

To investigate the behaviour of methyl halide fluxes throughout the day diurnal measurement campaigns were conducted. Fluxes were measured for one collar of each collar pair (normally

choosing the stronger emitting one) every 4.8 h 5 times at Hollands Farm and 6 times at Heckie's Hole. At Heckie's Hole the time of day of the first and last measurement cycle therefore coincided giving the opportunity to check for day-to-day variability. This was not possible for Hollands Farm due to a restriction in time and resources.

3.3.2.3 Testing of chamber size and enclosure time

Chamber size and enclosure times can potentially alter methyl halide fluxes (Section 2.1.1) and should be considered when interpreting the results of a measurement campaign employing static enclosure chambers. These parameters should also be considered when comparing results between studies. Therefore, on three occasions a series of measurements were conducted with increasing enclosure times, and on one occasion decreasing chamber sizes. Enclosure times included 2.5, 5, 10, 20, 30 and 40 min and always started with the shortest time increasing to the longest time at the end. Between each enclosure several minutes were left for the plants to recover. The enclosure size study was conducted with two different size chambers on each of two collars. First a collar was enclosed for 10 min with a 21.5 cm tall chamber (27 L volume), then left open for several minutes and again enclosed for 10 min with a 63.5 cm tall chamber (80 L volume).

3.3.3 Controlled experiments

3.3.3.1 Shading experiment

On the 31st May 2009 a separate field experiment to study the influence of sunlight was carried out at Heckie's Hole. First, fluxes from each collar pair were measured in the usual fashion with a transparent 21.5 cm high enclosure for 10 min. Then the measurement was repeated, with both the chamber and the light sensors beneath a 95 cm long × 62 cm wide × 47 cm high scaffold covered with a semitransparent green tarpaulin net. Finally the scaffold was covered by a blanket and the first collar of each pair was measured for a third time in total darkness (Figure 3.8). This was repeated for all four collar pairs in the salt marsh. The aim was to reduce the incident sunlight whilst maintaining the temperature inside the chamber as constant as possible, and therefore to distinguish between sunlight and air temperature as drivers for methyl halide fluxes. Due to problems with the analytical equipment at the time only CH₃Br fluxes were quantified.



Figure 3.8: Scaffold in salt marsh covered with blanket.

3.3.3.2 Vegetation removal experiment

On the 16th and 18th June 2009 at Hollands Farm and Heckie's Hole, respectively, above-ground vegetation from all salt marsh collars was removed using scissors and collected to determine the mass and make-up of the vegetation. In the laboratory it was sorted by species and dead plant material was removed. The sorted plant material was then oven dried at 70 °C as described in Section 3.3.1.2. Methyl halide fluxes were measured—where possible before and—immediately after removal and then on two more occasions at fortnightly intervals. Between measurement days the collars were covered with a black landscaping textile to slow vegetation regrowth and any new vegetation was removed before commencing measurements. Due to problems with the analytical equipment at the time only CH₃Br fluxes could be retrieved for the beginning of the experiment.

3.3.3.3 Greenhouse experiment

The greenhouse experiment was conducted to separate the influence of sunlight, temperature and time of day on methyl halide fluxes from salt marsh plants. Therefore the fluxes of several salt marsh plant species were artificially increased and the plants then subjected to differing light and temperature regimes to observe the relative increase or decrease of methyl halide

fluxes. Due to problems with the analytical equipment at the time only CH_3Br but not CH_3Cl could be determined.

During 2008 and 2009 intact specimens (i.e. with root systems) of several plant species were collected from both Heckie's Hole and Hollands Farm. Each plant was washed thoroughly to separate soil residues from the root system and to remove any parts of unwanted species. Then several specimens of each species were replanted in fresh acid-washed sand in 25 cm diameter, 25 cm high circular pots and grown in an unheated greenhouse until the start of the experiment. Altogether nine pots were used in the experiment: 4 pairs of replicates and another pot, and were regularly watered with a solution containing commercial fertilizer, potassium bromide and sodium chloride. The addition of halide ions was discontinued one month prior to the start of the experiment since preliminary tests showed that the fluxes were too high to measure with the available equipment, and so only one further addition of bromide was made, on the day before commencing flux measurements.

Of the nine pots used in this experiment two contained bare acid-washed sand, one *Agrostis gigantea*, two *Triglochin maritima*, two *Plantago maritima* and two which were mixtures of *Armeria maritima* and *Puccinellia maritima*.

The greenhouse in which the experiment was conducted was fully temperature controlled. Between 4:30 am and 8:30 pm daylight passing through the glass ceilings and walls of the glasshouse was supplemented with artificial light when the PAR level inside the glasshouse fell below $800 \mu\text{mol m}^{-2} \text{s}^{-1}$ for more than 5 min.

The enclosure used for the flux measurements consisted of two parts. The base was made of a 40 cm diameter 20 cm high, opaque PVC pipe which was glued on its bottom to a circular 5 mm thick PVC sheet of the same diameter with any gaps sealed with silicon sealant. On top of the base a fitting flange of the same inner diameter was glued in place, fastened with four M6 screws and again treated with silicone sealant to seal any gaps. The top part was a 40 cm diameter, 41.5 cm high ground chamber as described in Section 2.1.2.

For flux measurements the individual pots were placed inside the base and the chamber was enclosed for 2.5 min using bulldog clips to fasten the two parts together. During the enclosure time PAR, total solar radiation and chamber temperature were recorded automatically. Air pressure and air temperature were measured, the former using an aneroid barometer (type M. 1991/a, Mechanism Limited, Croydon, UK).

The experimental regime was as follows (Table 3.1). On day 0 of the experiment the pots were moved into the temperature-controlled greenhouse. There the temperature was held for 2 d at 20°C to allow the plants to acclimatise. The following 2 d the temperature remained at 20°C .

On each of these days, 3 sets of measurements were carried out. Starting at approximately 11 am on day 2 all 9 pots were enclosed for 2.5 min. After the last enclosure was complete all pots were placed underneath the scaffold described in Section 3.3.3.1, covered with a blanket. The plants were held in darkness for ca. 10 min and then the enclosure measurements were repeated in the same order. However this time the top of the enclosure chamber was wrapped in an opaque plastic bin liner. This second set of enclosures typically finished before 1 pm. The third set of enclosure measurements was conducted at midnight. Working under torch light the plant pots were enclosed for 2.5 min in the same order as before. On day 3 of the experiment all three sets of daily measurements were repeated and on day 4 the temperature was raised to 25 °C. The plants were given 2 d to acclimatise and on days 6 and 7 the three sets of daily experiments were repeated. On day 8 the temperature was raised to 30 °C and the plants acclimatised for 2 d. Then on days 10 and 11 the enclosure measurements were conducted and on day 12 the temperature was reset to the original 20 °C. The plants were given 3 d to acclimatise and the last set of enclosures were conducted on days 15 and 16. Finally, on day 17 the plants were cut off, washed, weighed, oven dried at 70 °C, reweighed and sent to Germany for XRF-analysis (Section 2.3.2).

The average concentration value derived from the two bare sand pots was used as a blank against which all other concentrations were measured to calculate the respective CH_3Br fluxes. Flux values were calculated per weight of dried plant material ($\text{ng g}^{-1} \text{ h}^{-1}$).

Table 3.1: Timetable of greenhouse experiment.

Day	Activity
0-1	Plants are moved into greenhouse and are acclimatising at 20 °C
2-3	Daily measurements at 20 °C in daylight, artificial darkness and during night time
4-5	Plants acclimatising at 25 °C
6-7	Daily measurements at 25 °C in daylight, artificial darkness and during night time
8-9	Plants acclimatising at 30 °C
10-11	Daily measurements at 30 °C in daylight, artificial darkness and during night time
12-14	Plants acclimatising at 20 °C
15-16	Daily measurements at 20 °C in daylight, artificial darkness and during night time
17	Removal of above-ground plant material

3.4 Results and Discussion

Where appropriate the results for both salt marshes are presented together to highlight similarities and differences between the two sites. Results of site characterisation are

presented first followed by the seasonal and diurnal fluxes measured. Finally the results of the smaller systematic experiments are presented and discussed.

3.4.1 General characterisation

3.4.1.1 Soil

All soil samples from Heckie's Hole can be classified as silty loam with an SOM content between 10.3 and 22.2 % (w/w) (Figure 3.9 and Table 3.2). This is in agreement with previous findings by Drewer et al. [2006] for the same salt marsh who reported that all soil samples were classified as silty loam with SOM content ranging between 18–21 % in the first 10 cm.

In contrast, soils from Hollands Farm (Figure 3.9 and Table 3.3) had much higher fractions of sand and were, with two exceptions, classified as sandy loam. Their textures were also more variable due to the greater variation in the physical environment. The clay fraction did not exceed 5 %. The sand fraction varied between 39–79 % with the lowest percentage found at collar pair L3 just below the first terrace edge whilst the highest sand fractions were found at position L2. SOM was significantly lower (one tailed t -test, $P < 0.05$) at Hollands Farm than at Heckie's Hole ranging between 1.8 to 4.4 % (w/w). Here the upper marsh contained between one and a half times to twice the organic matter found in the lower marsh, the notable exception being the relatively high SOM contents at L3.

At Heckie's Hole at each sampling location there was a clear decrease in SOM with depth of up to 6 % from the 0–5 cm to 10–15 cm samples. The SOM content for the four sampling locations was fairly uniform apart from at U2 where there was a lower SOM content. At Hollands Farm clear SOM content relationships with depth are not apparent as the SOM content is very low.

A similar pattern was observed for soil water content. Volumetric and gravimetric water contents of the soils at Hollands Farm were approximately 30 % lower than at Heckie's Hole. At all sampling positions in both marshes the water content in the uppermost 5 cm was the highest and decreased with depth. There is good general agreement between the results of the more detailed one-off study with the simpler surface water content measurements made parallel to the seasonal flux measurements next to each individual collars (Figure 3.10). Any difference between the normal range of values obtained throughout the flux measurement campaign and the one-off study could easily be due to spatial variations in soil conditions between the differing sampling locations. The variation in soil water content in 2 years at Heckie's Hole is remarkably small (with the exception of collar U1b) being no more than

Table 3.2: Soil physical properties at different locations at Heckie's Hole in samples collected on the 3rd August 2009. Percentages of clay, silt and sand are given as % (V/V) whilst SOM content is given as % (w/w). Sediment water content (WC) is given as volumetric water content (% $V_{\text{water}}/V_{\text{bulk soil sample}}$) and gravimetric water content (% $m_{\text{water}}/m_{\text{fresh soil sample}}$).

Location	Depth (cm)	Clay (%)	Silt (%)	Sand (%)	SOM (%)	DBD (kgm^{-3})	WC (V %)	WC (w %)
L1	0-5	18	76	6	22.2	484	79	62
L1	5-10	18	72	10	19.7	516	77	60
L1	10-15	18	74	8	16.9	596	73	55
L2	0-5	18	74	8	21.3	505	73	59
L2	5-10	17	75	8	18.7	568	73	56
L2	10-15	18	74	8	17.8	622	73	54
U1	0-5	19	74	7	22.3	452	80	64
U1	5-10	18	73	9	19.0	500	74	60
U1	10-15	17	74	9	16.5	598	73	55
U2	0-5	15	71	14	14.4	377	83	69
U2	5-10	15	73	12	12.4	390	81	68
U2	10-15	16	76	8	10.3	404	83	67

Table 3.3: Soil physical properties for different locations at Hollands Farm in samples collected on the 4th August 2009. Percentages of clay, silt and sand are given as % (V/V) whilst SOM content is given as % (w/w). Soil water content (WC) is given as volumetric water content (% $V_{\text{water}}/V_{\text{bulk soil sample}}$) and gravimetric water content (% $m_{\text{water}}/m_{\text{fresh soil sample}}$).

Location	Depth (cm)	Clay (%)	Silt (%)	Sand (%)	SOM (%)	DBD (kgm^{-3})	WC (V %)	WC (w %)
S+L1	0-5	3	24	73	1.8	1410	56	28
S+L1	5-10	3	31	66	2.0	1410	46	24
S+L1	10-15	3	28	69	2.0	1510	46	23
L2	0-5	3	32	65	2.0	1330	47	26
L2	5-10	3	29	68	2.0	1430	44	23
L2	10-15	2	19	79	2.0	1490	46	24
L3	0-5	5	56	39	3.8	980	59	38
L3	5-10	4	43	53	2.6	1280	50	28
L3	10-15	3	40	57	2.4	1270	50	28
U1+U3	0-5	2	28	70	3.2	1050	53	33
U1+U3	5-10	3	30	67	3.6	1200	48	29
U1+U3	10-15	3	35	62	3.6	1160	45	28
U2	0-5	3	33	64	4.4	935	58	38
U2	5-10	3	42	55	3.8	1260	47	27
U2	10-15	2	29	69	2.0	1310	44	25

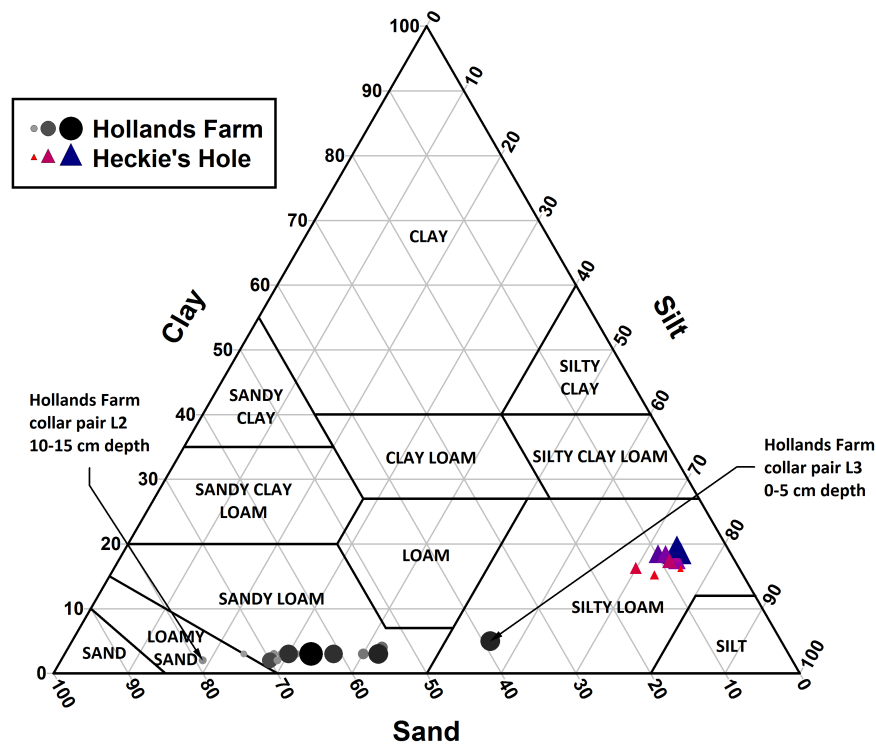


Figure 3.9: Soil texture characterisation for Heckie's Hole and Hollands Farm. Triangles and circles represent measurements taken from Heckie's Hole and Hollands Farm respectively. The size and colour of the symbols represents the SOM content. SOM values for Heckie's Hole range from 10.3 % (small red) to 22.3 % (large blue). SOM values for Hollands Farm range from 1.8 % (small light grey) to 4.4 % (large black). Soil texture triangle drawn after USDA classification [Soil Survey Division Staff, 1993]

7.4 % (w/w) (and 14 % (w/w) for U1b) (Figure 3.10a). In contrast the soil water content for the collars at Hollands Farm varied by 6.1–17 % (w/w). This greater variation is most likely due to the higher proportion of sand and lower soil organic matter (SOM) content of the soil at Hollands Farm reducing the water-holding effectiveness.

The higher clay content and (partially as a result of this) the higher water content in Heckie's Hole together with its greater age would have allowed the marsh to accumulate more organic matter and to start producing autochthonous soil material. In contrast, the low clay content and the more active nature and much younger age of most of the marsh at Hollands Farm has prevented any appreciable development of new soil material apart from at collar L3 which had a higher SOM content and lower percentage of sand.

The different soil characteristics of the two salt marshes have implications for soil microbial activity. Specifically the higher organic matter and higher clay content of the soils at Heckie's Hole would have provided a better water holding capacity and as an effect of this a higher reduction potential and more moderated soil temperatures than the soils at Hollands Farm.

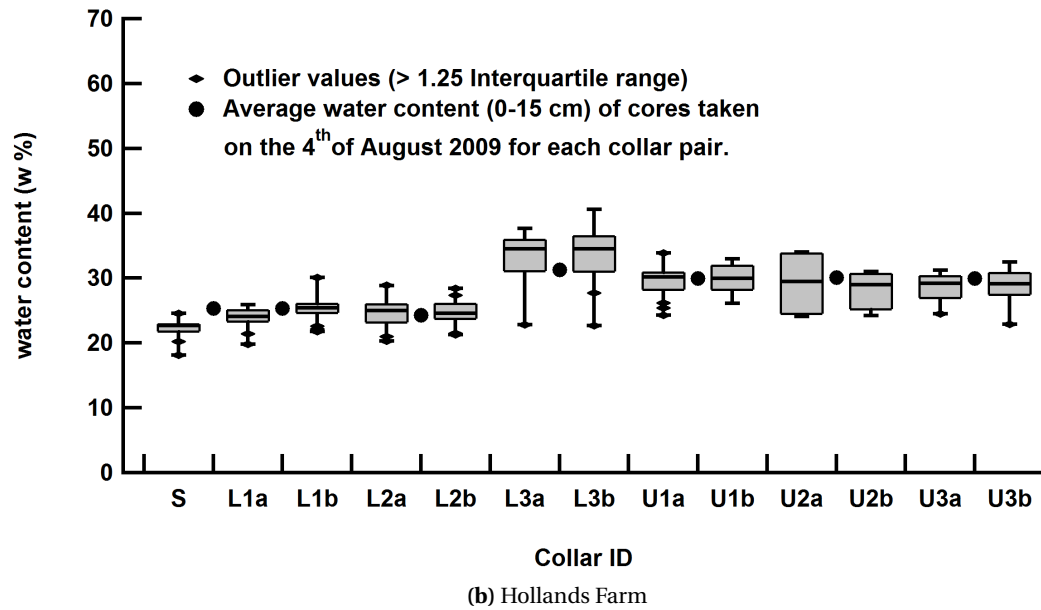
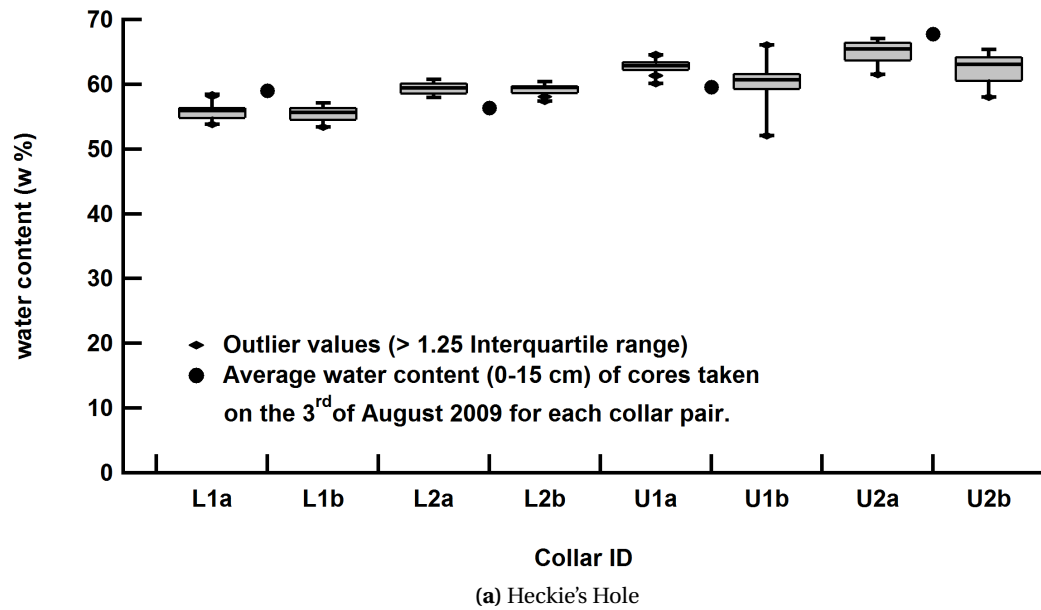


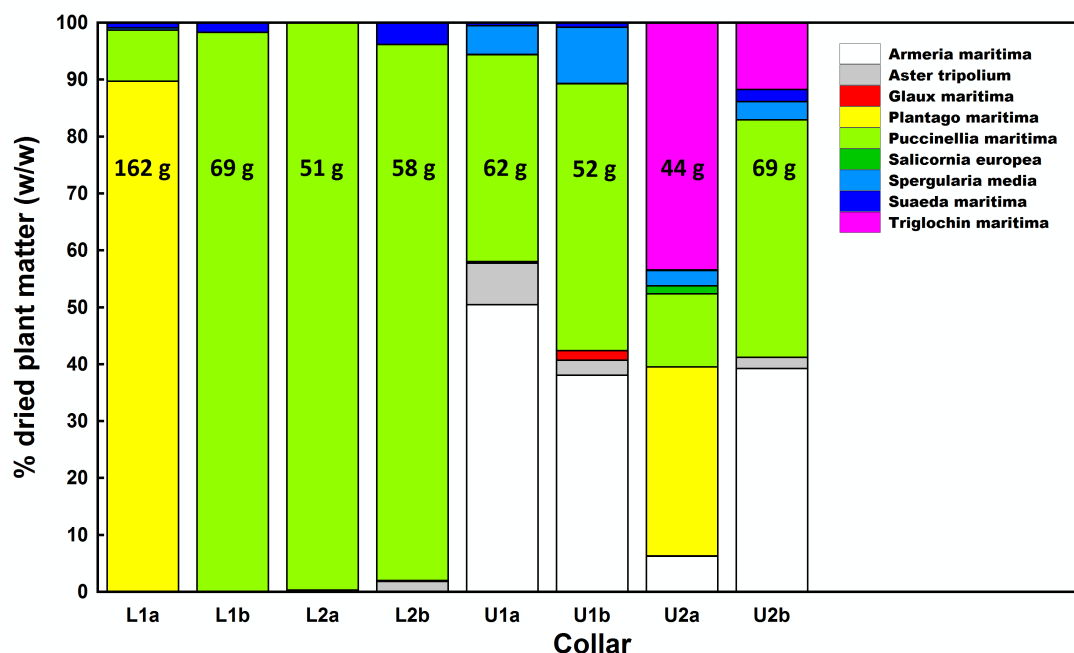
Figure 3.10: Statistical distribution of the gravimetric water content of soil samples ($n \approx 21$ samples per collar) taken at 0–8 cm depth during seasonal flux measurements. The thick horizontal bar inside each box marks the median value and the upper and lower boundaries of the box the 3rd and 1st quartile respectively. The whiskers give the full range of values. Outlier values are also shown. For comparison, average values from the more detailed soil analysis ($n = 3$ samples per collar pair, taken at 0–5 cm, 5–10 cm and 10–15 cm depth) carried out in both salt marshes during August 2009 are shown between the individual measurements.

The acid groups of the SOM at Heckie's Hole would furthermore have lowered the soil pH considerably and most importantly the SOM would act as an energy source to support a diverse soil micro-organism community. In comparison to Heckie's Hole the soils at Hollands Farm would appear to be almost devoid of such microbial activities. Therefore, if soil micro-organisms do indeed take up methyl halides then their number and effect is expected to be greater at Heckie's Hole and probably negligible in Hollands Farm. On the other hand, if warmer, drier, more oxygenated conditions favour oxidation of methyl halides by soil micro-organisms then uptake should be more noticeable at Hollands Farm. Furthermore the greater fluctuation of water content at Hollands Farm could have led to higher emissions during long drought periods as the halide concentrations inside the soil and subsequently the plants would have risen.

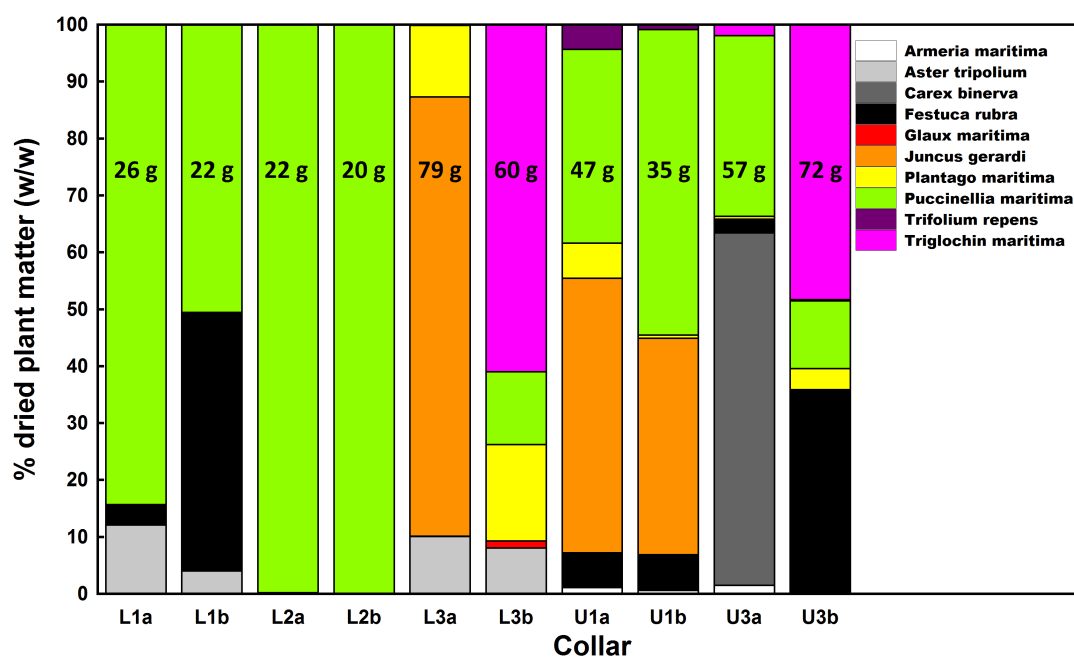
3.4.1.2 Vegetation

As shown in Figure 3.11a *Puccinellia maritima* accounted for 99.4 to 99.6 % by mass of all the living vegetation in three of the four lower salt marsh collars in Heckie's Hole whilst it only accounted on average for 34.4 % of the vegetation in the upper marsh. *Armeria maritima* accounted for another 33.5 % in the upper marsh but was absent from the lower marsh. These two species alone accounted for three-quarters of the average vegetation mass for all sample collars. An exception was collar L1a which had been placed around an aggregation of *Plantago maritima*. This succulent species did not cover large areas of a salt marsh but instead grew as small (<0.5 m²) but very dense patches in the lower marsh area (Figure 3.4a), explaining the high overall mass of vegetation in the collar. A species with a similar growth pattern is *Triglochin maritima* which sometimes formed dense clumps but also occurred as part of a mixed carpet with other species over wide areas in the upper marsh. Together these four species accounted for most of the vegetation at Heckie's Hole. Apart from collar L1a the density of vegetation was rather uniform throughout the whole of the marsh. Previous work at Heckie's Hole [Drewer et al., 2006; Drewer, 2007] identified the main grass species as *Festuca rubra* rather than *Puccinellia maritima* due to a different identification of the plant species in question. In this work no *Festuca rubra* was identified in the collars at Heckie's Hole.

In comparison the vegetation at Hollands Farm was more diverse (Figure 3.11b). The lower parts of the pioneer zone (collar pairs L1 and L2) are dominated by a sparse cover of the salt-tolerant grasses *Puccinellia maritima* and *Festuca rubra*. *Aster tripolium* occurred in the hollow and hummock area represented by collars L1a and L1b (Figures 3.7b and 3.7c) but at the time of vegetation collection was not fully grown and might therefore be underestimated. The vegetation in collar L3a and L3b was three to four times more dense than at L1 and



(a) Vegetation composition in collars at Heckies Hole in vegetation harvested from each collar on the 18th June 2009.



(b) Vegetation composition in collars at Hollands Farm in vegetation harvested from each collar on the 16th June 2009.

Figure 3.11: Vegetation composition for Heckie's Hole and Hollands Farm. The percentages are based on the dry mass of plant material excluding any dead plant material. The number in each column is the total dry mass of plant material for the collar. No information on vegetation mixtures for collars U2a and U2b in Hollands Farm is available.

L2. Vegetation in L3a was dominated by *Juncus gerardi* which made up three-quarters of vegetation with the remainder being *Plantago maritima* and *Aster tripolium*. Vegetation in collar L3b consisted of 60 % *Triglochin maritima* and the rest comprised *Plantago maritima*, *Aster tripolium* and *Puccinellia maritima*. L3b was therefore strongly dominated by succulent plants which made up almost 90 % of the vegetation cover.

In the upper marsh U1a and U1b had very similar vegetation compositions being dominated by a mixture of *Juncus gerardi* and *Puccinellia maritima*. Collar pair U3, which is located within a few metres of collar pair U1, was specifically chosen because of its differing vegetation from the latter. Collar U3a was covered by 60 % *Carex binerva* and 30 % *Puccinellia maritima* whilst collar U3b was covered by a mixture of 50 % *Triglochin maritima*, 35 % *Festuca rubra* and 10 % *Puccinellia maritima*. The overall mass of plant material for these four collars varied widely ranging from 35 g to 72 g reflecting the very different physiognomy of the plants enclosed.

No vegetation analysis was undertaken for collar pair U2. However the area where the collars were located can be characterised as a closely cropped lawn-like sward that is dominated by graminoid (grass) vegetation [Hansom, 2003; Scottish Natural Heritage, retrieved 16th November 2009]. The area is heavily grazed by cattle and is essentially a freshwater habitat that is only inundated with salt water at the highest annual tides. It therefore does not share many of the species found in the lower parts of Hollands Farm.

Overall *Puccinellia maritima* was again one of the most widespread species accounting on average for 50 % of the vegetation cover at Hollands Farm but the remainder of the vegetation was made up of a more varied mixture of species.

The total above-ground plant mass and vegetation mixture reported here is only a snapshot. In the 2 years field monitoring programme the vegetation mixture was observed to change during the growing season. Different species grow and die off at different times and so the overall vegetation make-up varies depending on the time of sampling. Furthermore the pioneer zone at Hollands Farm (represented by collar pairs L1 and L2) became more densely vegetated over the duration of the measurement campaign.

3.4.1.3 Plant halogen content

The data shown in Table 3.4 were derived by measuring a mixture of samples taken from several locations at both Heckie's Hole and Hollands Farm on the 6th and 7th July 2009 (except *Salicornia europea* which was only collected in Heckie's Hole). In interpreting the data for both salt marsh sites and the entire measurement period it is assumed that the concentrations

of bromine and chlorine were spatially uniform for a species within and between sites. It is also implicitly assumed that the concentrations were more or less temporally uniform as well. Not all species encountered at both sites were analysed due to a scarcity of resources.

Table 3.4: Bromine and chlorine concentrations measured by XRF in above-ground plant material from Heckie's Hole and Hollands Farm. The last column represents the chlorine to bromine mass ratio. n.a. = not available

Species	Br ($\mu\text{g g}^{-1}$)	Cl (mg g^{-1})	Cl/Br mass ratio
<i>Armeria maritima</i>	255	26.0	102
<i>Aster tripolium</i>	333	63.0	189
<i>Carex binerva</i>	55.3	9.30	168
<i>Juncus gerardi</i>	85.5	16.2	189
<i>Plantago maritima</i>	461	81.5	177
<i>Puccinellia maritima</i>	77.0	11.0	143
<i>Salicornia europea</i>	782	192	245
<i>Spergularia media</i>	912	87.4	96
<i>Suaeda maritima</i>	681	146	214
<i>Triglochin maritima</i>	213	n.a.	-
mean Cl/Br mass ratio			169

Bromine concentrations for grass-like plants, such as *Carex binerva*, *Juncus gerardi* and *Puccinellia maritima*, were all below $100 \mu\text{g g}^{-1}$ and chlorine concentrations ranged from $9\ 300$ to $16\ 200 \mu\text{g g}^{-1}$. On the other hand bromine and chlorine levels in small succulent plants such as *Salicornia europea*, *Spergularia media* and *Suaeda maritima* reached up to $912 \mu\text{g g}^{-1}$ and $192\ 000 \mu\text{g g}^{-1}$ respectively. Bromine and chlorine levels for larger succulent plants, including *Aster tripolium*, *Plantago maritima*, *Triglochin maritima* as well as *Armeria maritima*, lay between these two extremes. There was generally a good correlation between the total chlorine and bromine concentrations (Figure 3.12). The mean Cl/Br mass ratio of 169 found in the plants is lower than the Cl/Br-mass ratio of sea water (~ 270) [Wiberg, 1995]. Assuming sea water was the main source of halogen inside these plants, the lower Cl/Br-mass ratio suggests that there was a preference for bromine accumulation compared to chlorine.

The chlorine concentrations of *Triglochin maritima* and the bromine and chlorine concentrations of *Festuca rubra* were not measured but were estimated as follows in order to calculate the total halogen content of vegetation in the collars. The chlorine concentration for *Triglochin maritima* was calculated as $25\ 400 \mu\text{g g}^{-1}$ from the known bromine concentration and the Cl/Br mass ratio given in Figure 3.12. For *Festuca rubra* the halogen content was estimated from the average of the other three grass-like plants, *Carex binerva*, *Juncus gerardi* and *Puccinellia maritima*, as $73 \mu\text{g g}^{-1}$ Br and $12\ 200 \mu\text{g g}^{-1}$ Cl.

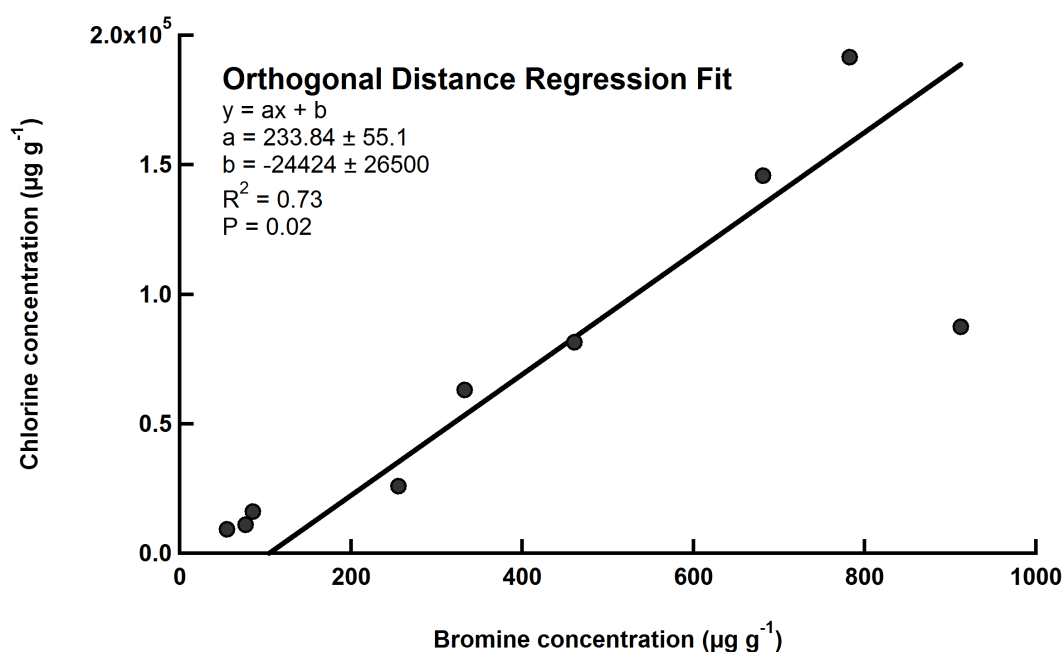


Figure 3.12: Linear relationship between chlorine and bromine concentration in above-ground vegetation.

By multiplying the individual halogen concentrations for the different species with their individual dry weights in the measurement collars the total bromine and chlorine mass in above-ground vegetation for each collar was derived (Table 3.5). The highest total bromine and chlorine mass of all the collars was found in collar L1a at Heckie's Hole with almost 70 mg of total bromine and more than 12 g of total chlorine due to substantially higher dry biomass and also relatively high bromine and chlorine concentrations of the dominant species, *Plantago maritima*. There was a clear distinction in halogen content at Heckie's Hole between the lower and upper marsh. Total bromine at L1b, L2a and L2b ranged between 4–6.1 mg and total chlorine reached a maximum of 1 000 mg. In the upper marsh bromine and chlorine were on average 2^{1/2} and twice this value respectively.

In contrast the halogen mass in above-ground vegetation at Hollands Farm was generally lower. Whilst the vegetation in most collars did not exceed 5 mg of bromine and 822 mg of chlorine three collars had halogen masses similar to the upper marsh at Heckie's Hole. Collars L3a and L3b had very different vegetation compositions but had very similar masses of both bromine and chlorine. Collar U3b at Hollands Farm also had a higher halide mass due to its higher vegetation mass. In Section 3.4.3 these findings are used to interpret measured methyl halide fluxes. However, assuming that vegetation halogen mass is an indicator for methyl halide fluxes, collars at Heckie's Hole are expected to emit considerably larger amounts of methyl halides than collars at Hollands Farm, in particular collar L1a in Heckie's Hole which

Table 3.5: Total bromine and chlorine mass of above-ground vegetation in the salt marsh collars. For collars containing *Triglochin maritima* and *Festuca rubra* the values shown outside brackets include the estimated contributions of these plants and the values in brackets represent directly measured values only.

Heckie's Hole			Hollands Farm		
Collar	Total Br (mg)	Total Cl (mg)	Collar	Total Br (mg)	Total Cl (mg)
L1a	69.8	12 300	L1a	2.8 (2.7)	444 (433)
L1b	6.0	918	L1b	1.8 (1.1)	294 (175)
L2a	4.0	569	L2a	1.7	242
L2b	6.1	999	L2b	1.5	222
U1a	14.2	1 660	L3a	12.5	2 300
U1b	12.5	1 390	L3b	14.7	2 180 (1 260)
U2a	13.4	2 020 (1 540)	U1a	4.8 (4.6)	822 (787)
U2b	14.4	1 730 (1 520)	U1b	2.9 (2.8)	475 (448)
			U3a	4.1 (4.0)	622 (578)
			U3b	11.2 (9.4)	1 520 (315)

has a bromine and chlorine content almost an order of magnitude higher than the other collars.

3.4.2 Influence of enclosure time and chamber size on methyl halide fluxes

Of the five enclosure time series conducted for CH_3Br , three showed a sharp reduction in net CH_3Br emissions within the first 5 min of an enclosure, followed by a more gradual decline (for an example see Figure 3.13a). In one study, net emissions gradually declined at a steady rate and one collar showed no change in emissions with increasing enclosure time. To determine if net CH_3Br fluxes declined significantly with longer enclosure times, all measured fluxes from the enclosure time experiments were normalised against the respective fluxes at 2.5 min enclosure time for the individual collars. Then a one-tailed t -test was applied to the two data sets of normalised fluxes at 2.5 and 10 min enclosure duration. There was a significant decline in net fluxes with time ($P = 0.028$) and by applying a linear regression fit to the normalised data for 2.5, 5 and 10 min enclosures and extrapolation to "0" min a ratio of "ideal" to measured fluxes of 1.5 ± 0.2 was calculated. That is, flux values derived from 10 min-enclosures multiplied by 1.5 yield the theoretical flux at "0" min.

Data from four enclosure time experiments were available for CH_3Cl (for an example see Figure 3.13b). However, the precision of CH_3Cl concentrations determined by GC is lower than for CH_3Br and full data sets are only available for the two displayed experiments. Following the same procedure as for CH_3Br no statistically significant difference between the

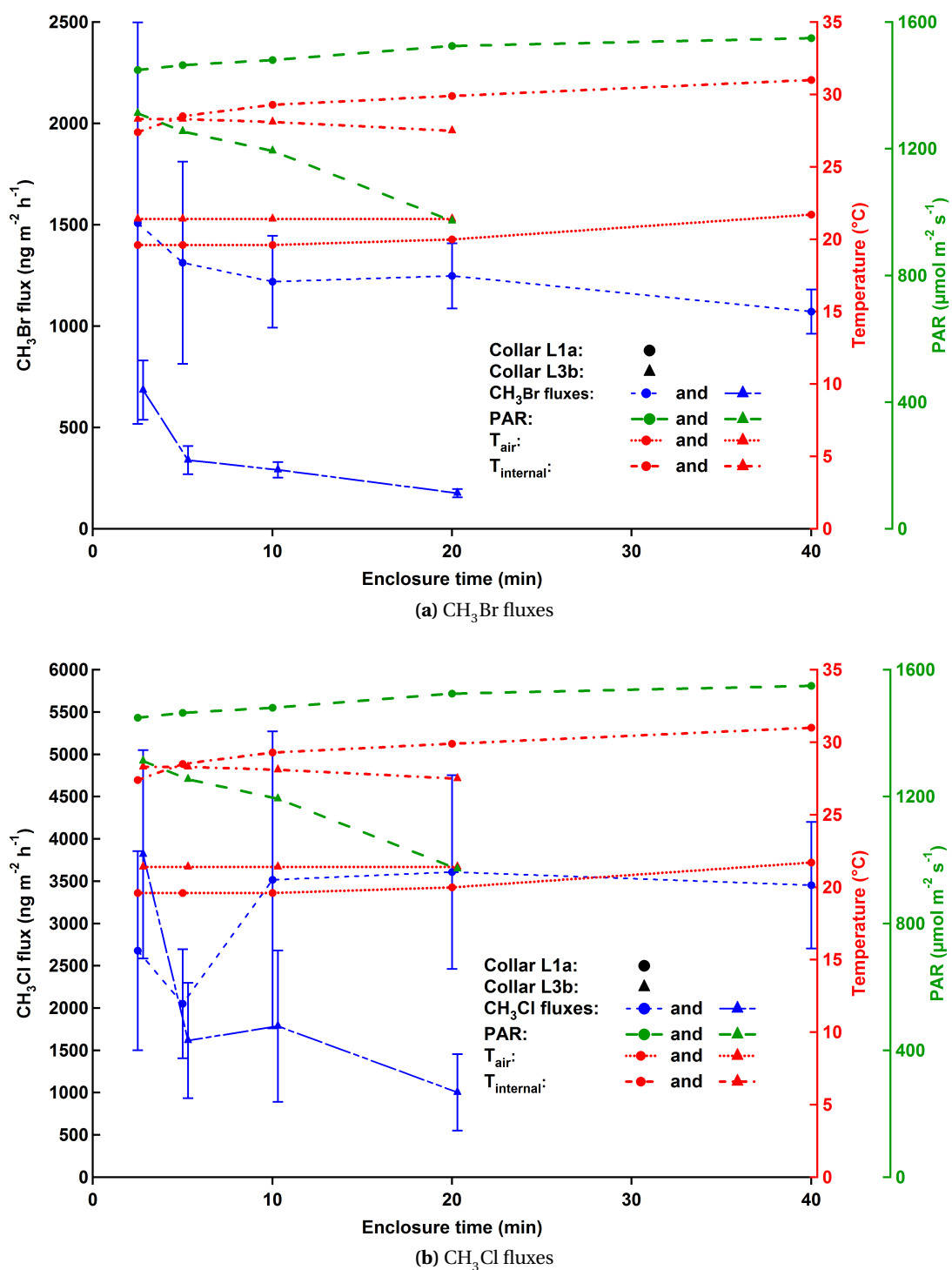


Figure 3.13: Two examples of enclosure time series of net methyl halide fluxes conducted at Hollands Farm on the 8th May 2008. Additional to methyl halide fluxes concurrent ambient air temperature and are drawn. Whiskers incorporate both analytical and sampling uncertainties.

2.5 and 10 min enclosure times was found and it has to be assumed that either there is no effect of enclosure times on net CH_3Cl fluxes or that CH_3Cl fluxes behave similarly to CH_3Br fluxes bringing the possible range of a correction factor from 1–1.5.

For the two chamber size studies conducted (Figure 3.14), only CH_3Br flux values were available and due to the sparsity of data no statistical analysis was performed. However,

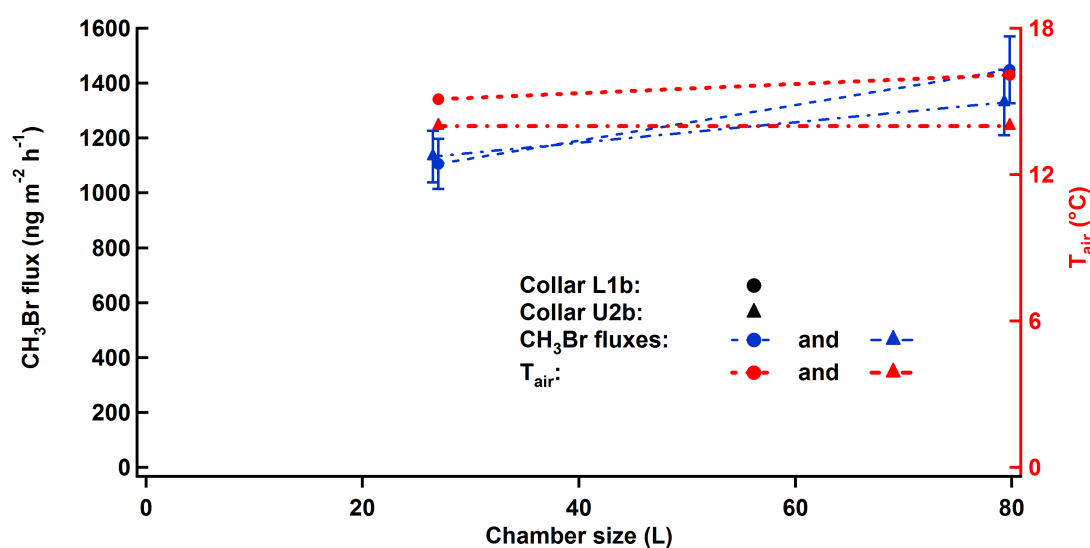


Figure 3.14: Two enclosure size experiments conducted at Heckie's Hole on the 3rd September 2007. Shown is the dependency of net methyl halide fluxes on chamber size. Whiskers incorporate both analytical and sampling uncertainties. The symbols marking flux magnitudes were slightly offset to facilitate legibility. Concurrent ambient air temperatures are also shown.

the displayed data suggest that measured net fluxes rise with larger enclosure sizes. This corroborates the findings from the enclosure time studies. Both increased chamber size and shorter enclosure times lower the concentration build-up during the length of an enclosure experiment and therefore are expected to result in a similar increase of methyl halide production (and/or methyl halide uptake) per unit of time. Unfortunately it is not immediately obvious how to convert the effect of increased chamber sizes to decreased enclosure times and more statistically relevant results are available from the enclosure time studies.

The flux measurements presented in the following sections do not include any correction factor for the discussed effect of enclosure time but the issue is considered for the final global scale-up.

3.4.3 Seasonal fluxes

Seasonal flux measurements are examined in two different ways. First the time series of seasonal flux patterns of CH_3Br and CH_3Cl and drivers are discussed in brief for the 2 yr monitoring program specifically examining temporal variations within and between the different years. Second the fluxes are analysed statistically with the environmental factors monitored to determine if and what is driving methyl halide fluxes.

In the presentation and discussion of results, each year was divided into a growing season (beginning of April to end of October) and a non-growing season (rest of the year). The distinction was made on grounds of observational evidence of plant growth.

Figures 3.15 to 3.30 show time series of seasonal net fluxes of both methyl halides at Heckie's Hole and Hollands Farm for the years 2007–2009 together with PAR, ambient air temperature at time of measurement and soil temperature for comparison.

Standard deviation values were calculated for all methyl halide fluxes presented here but were deliberately left out of some graphs to enhance legibility.

3.4.3.1 Variations in seasonal fluxes

CH_3Br fluxes at Heckie's Hole Figures 3.15 to 3.17 show all seasonal CH_3Br fluxes for all 8 collars together with the respective PAR levels, ambient air temperature and soil temperature for the years 2007, 2008 and 2009. From these figures the following observations can be made:

- Despite the differences in vegetation the annual net fluxes in the 8 collars for each calendar year followed a remarkably similar pattern. In contrast the differences in flux patterns from year to year for each collar during the 2 years of measurement were much more distinct. This indicates that the flux patterns for all 8 collars were determined not by the vegetation of the collars but rather by drivers such as temperature and sunlight.
- During 2007 CH_3Br emissions peaked several times between early July to mid-September. During 2008, however, emissions generally rose more steadily towards a maximum which for all but two collars was at the end of September (day 269) before declining during autumn and winter. During the part of the year 2009 for which measurements were taken CH_3Br emissions were often higher in spring compared to spring 2008 and reached levels similar to the previous years' peaks as early as the end

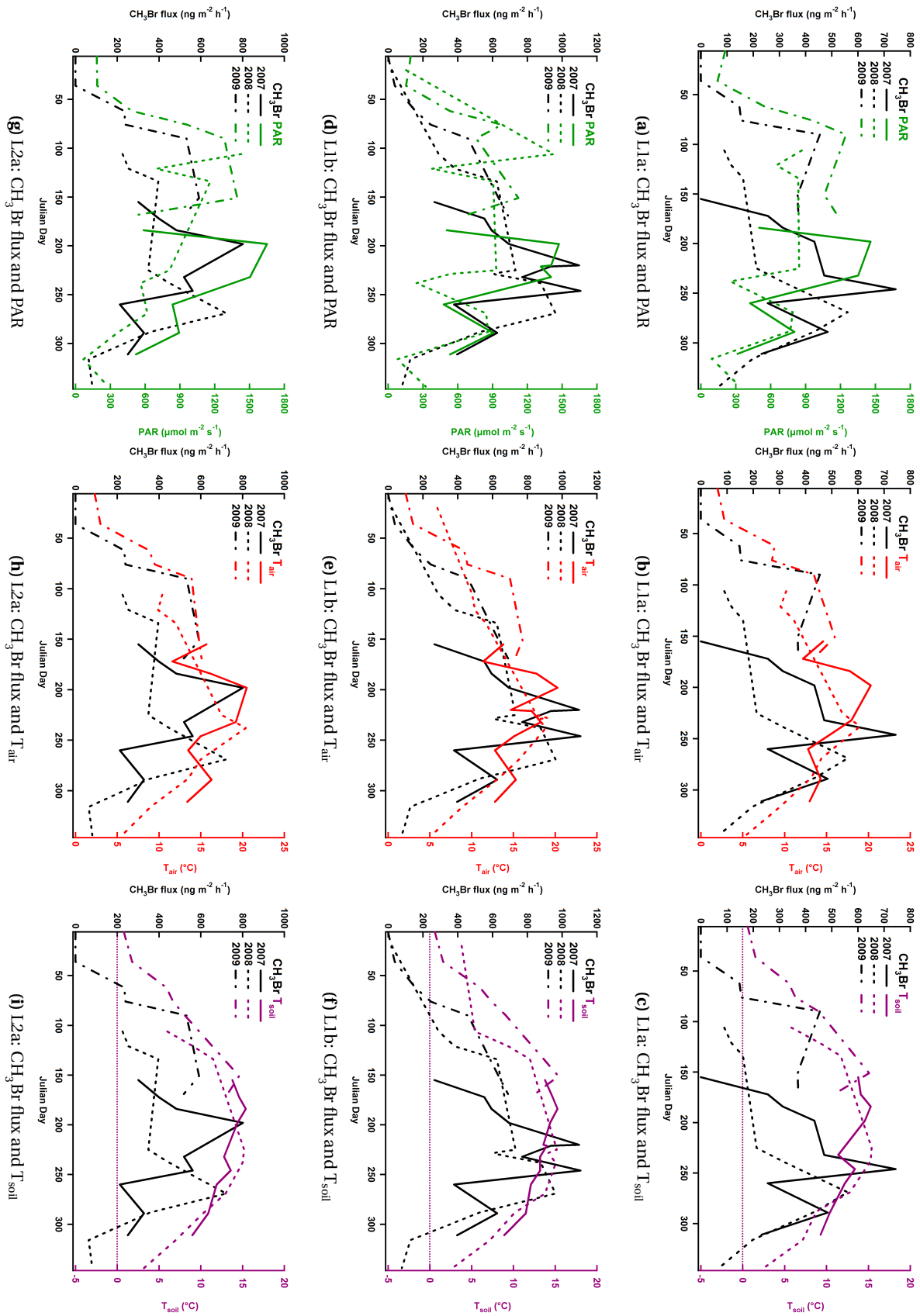


Figure 3.15: Comparison of seasonal net CH_3Br fluxes with possible drivers at Heckie's Hole for 2007, 2008 and 2009 for collars L1a, L1b and L2a. Note different y-axis scales for CH_3Br .

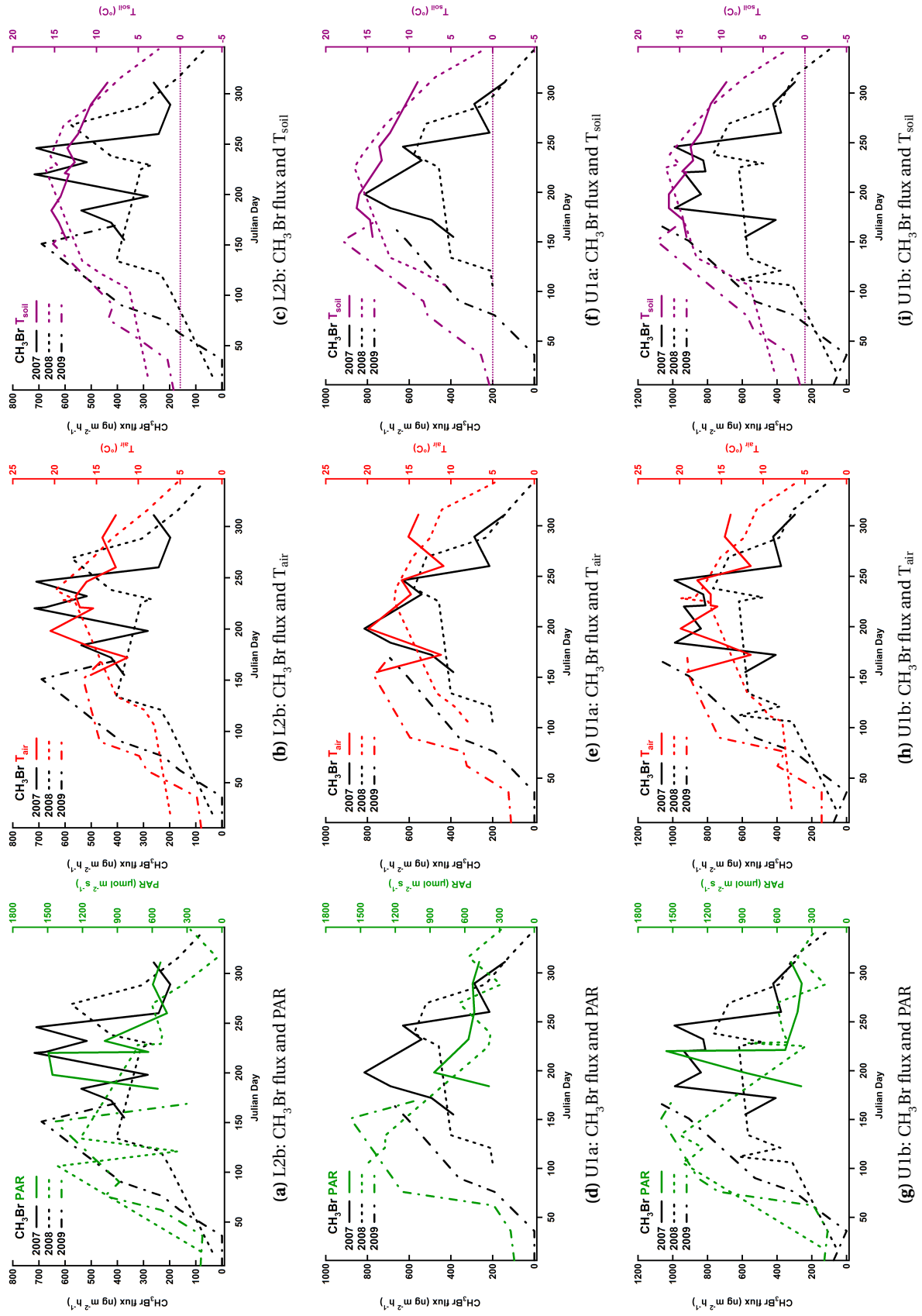


Figure 3.16: Comparison of seasonal net CH_3Br fluxes with possible drivers at Heckie's Hole for 2007, 2008 and 2009 for collars L2b, U1a and U1b. Note different y-axis scales for CH_3Br .

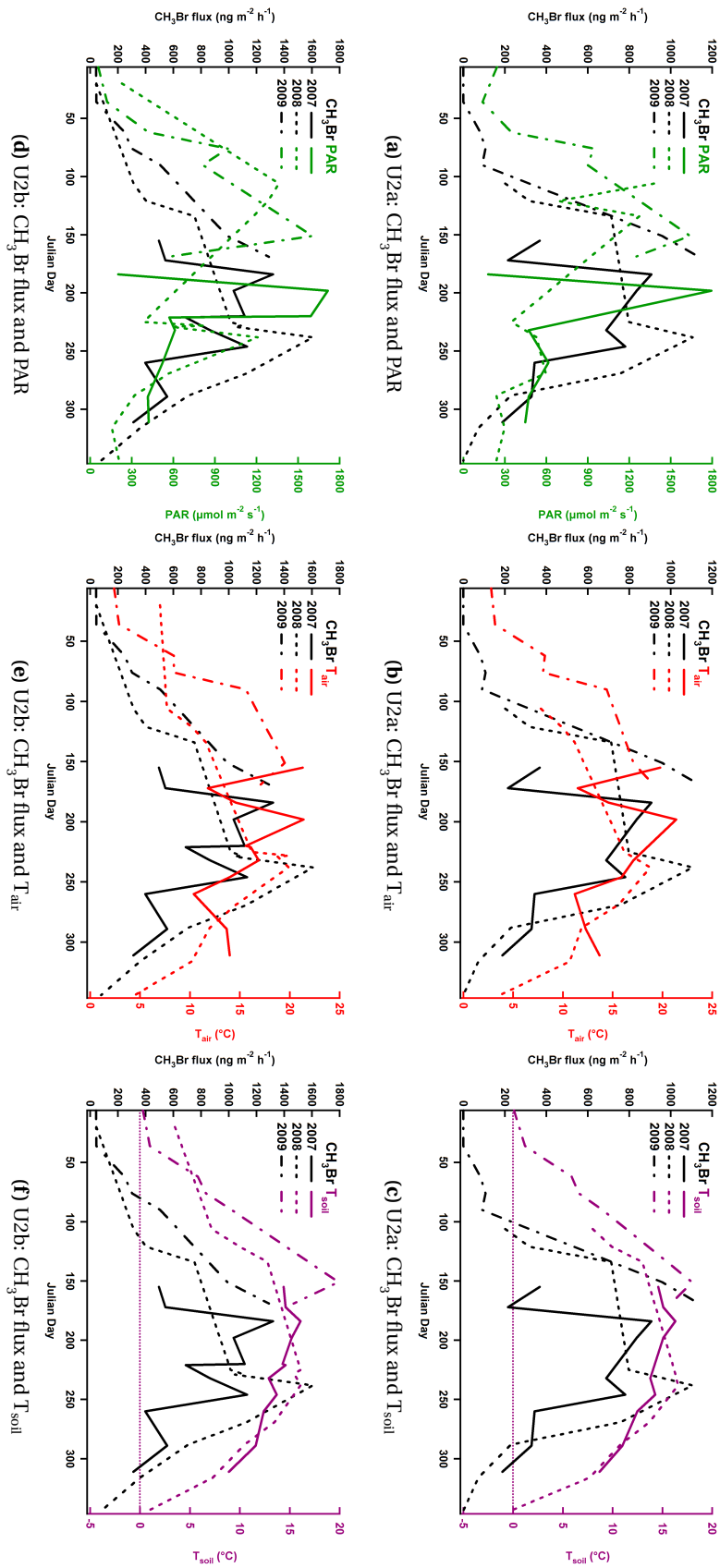


Figure 3.17: Comparison of seasonal net CH_3Br fluxes with possible drivers at Heckie's Hole for 2007, 2008 and 2009 for collars U2a and U2b. Note different y-axis scales for CH_3Br .

of March. The higher CH₃Br emissions in spring 2009 might be related to the relatively higher air and soil temperatures at that time compared to 2008.

- No net CH₃Br uptake was recorded. This suggests, but does not prove, that CH₃Br uptake processes in the soil are either very small or absent.
- Minimum fluxes for all but one collar were zero whilst maximum fluxes varied between 700–1600 ngm⁻²h⁻¹ (Table 3.6). Mean fluxes per collar ranged from 270–680 ngm⁻²h⁻¹ and were generally larger in the upper marsh.

Table 3.6: Mean, median, minimum and maximum net CH₃Br fluxes at Heckie's Hole for the entire measurement period. All flux values are given as ngm⁻²h⁻¹. The final column gives the number of measurements.

Collar	Mean	Median	Min	Max	number
L1a	274	255	0	745	25
L1b	517	574	0	1 106	30
L2a	355	349	0	802	25
L2b	337	297	0	717	30
U1a	356	361	0	815	25
U1b	529	527	0	1 100	31
U2a	450	329	0	1 136	25
U2b	682	623	45	1 608	30
All	445	389	0	1 608	221

- Net-fluxes during the growing season were on average 4.5 times the fluxes during the non-growing season.
- Statistical tests did not reveal any obvious correlation between plant species and flux strength. Collars with similar vegetation mixtures did not exhibit similar average fluxes. There was also no statistically significant correlation between total vegetation mass and average CH₃Br fluxes.
- CH₃Br emissions were not strongly associated with the Br content of plants since collar L1a (with the highest Br content) might be expected to produce significantly more CH₃Br than any other collar. Instead the lowest average CH₃Br emissions were from collar L1a.

In summary there was no explanation for the differences in strength of net emissions for the different collars through any of the measured factors. Ambient air temperature was the best indicator for changes in emissions for a collar over the year. However, physiological changes

in the vegetation beyond a crude measure of growing and non-growing season could not be accounted for. This could probably explain some of the differences between collars as described by Manley et al. [2006] who suggested that physiological events such as flowering to be responsible for temporary rises in methyl halide emissions by vegetation. Nevertheless, the patterns of fluxes for the different collars during each year were similar suggesting that an external factor is the main driver for CH_3Br emissions by plants.

CH_3Cl fluxes at Heckie's Hole Figures 3.18 to 3.20 show all seasonal CH_3Cl fluxes for all 8 collars together with the respective PAR levels, ambient air temperature and soil temperature for the years 2008 and 2009. From these figures the following observations can be made:

- The annual pattern of net CH_3Cl fluxes for the different collars in each year are very similar. In 2008 a local maximum in CH_3Cl fluxes often occurred during mid-May (day 134) and maximum annual CH_3Cl fluxes occurred at the end of September (day 269) coinciding with the maximum CH_3Br fluxes. For the beginning of 2009 where data are available fluxes started to rise above $0 \text{ ng m}^{-2} \text{ h}^{-1}$ as early as mid-March similar to the CH_3Br fluxes measured during this time.
- CH_3Br and CH_3Cl fluxes in each collar were strongly correlated in the lower salt marsh (R values ranged between 0.83–0.88, Table 3.7), whereas in the upper marsh a good correlation occurred only at collar U2b ($R = 0.78$). R values for two of the other three collars in the upper marsh were lower although still statistically significant.
- In 7 out of 8 collars CH_3Cl uptake was recorded (Table 3.7). This happened usually, but not exclusively, during the winter months when CH_3Cl production by plants was expected to be low.
- Minimum and maximum net fluxes ranged between $-1\,600$ – $0 \text{ ng m}^{-2} \text{ h}^{-1}$ and $1\,500$ – $6\,400 \text{ ng m}^{-2} \text{ h}^{-1}$ respectively. Mean fluxes per collar were 380 – $1\,500 \text{ ng m}^{-2} \text{ h}^{-1}$ and were strongly positively correlated with the total mass of *Puccinellia maritima* in each collar (Figure 3.21). Since *Puccinellia maritima* dominated collars L1b, L2a and L2b average fluxes from these collars were approximately double those from the other collars. This also meant that CH_3Cl fluxes, in contrast to CH_3Br fluxes, were generally higher in the lower marsh compared to the upper marsh.
- Fluxes during the growing season were on average 7.9 times higher than fluxes during the non-growing season. However, the highest rates of CH_3Cl uptake were recorded during the growing season. These were isolated occasions and of similar magnitude to uptake rates during the non-growing season.

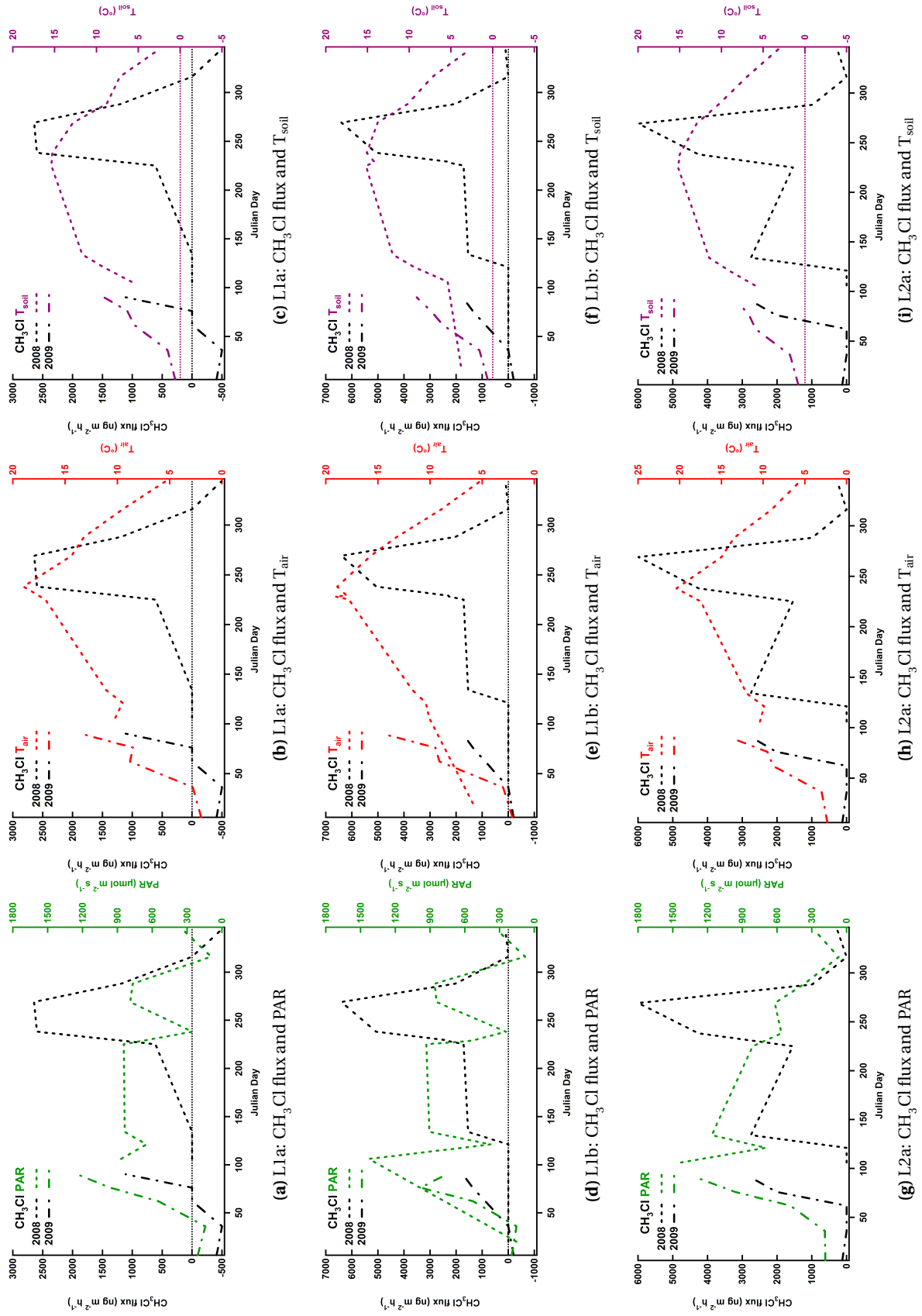


Figure 3.18: Comparison of seasonal net CH_3Cl fluxes with possible drivers at Heckie's Hole for 2008 and 2009 for collars L1a, L1b and L2a. Note different y-axis scales for CH_3Cl .

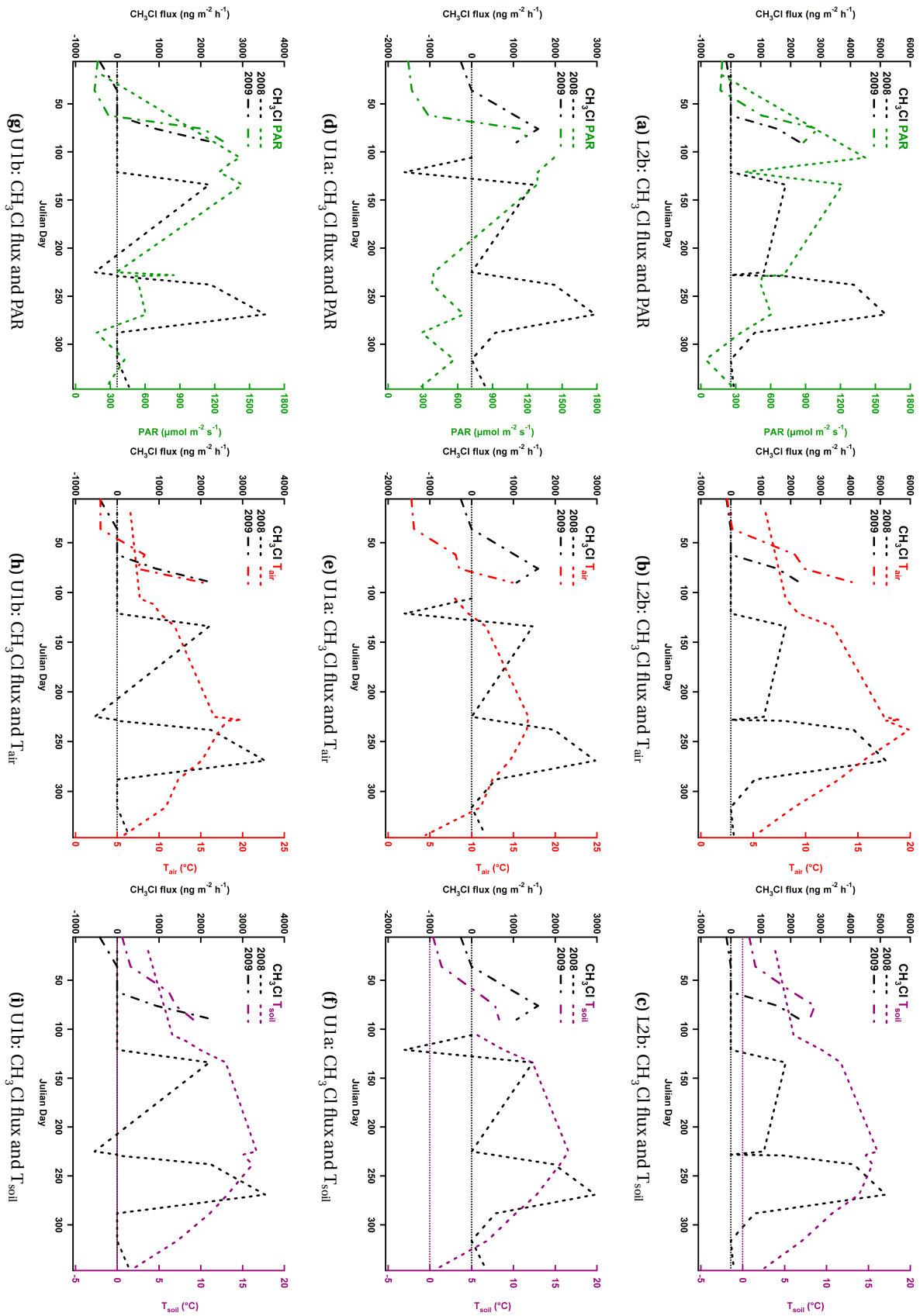


Figure 3.19: Comparison of seasonal net CH_3Cl fluxes with possible drivers at Heckie's Hole for 2008 and 2009 for collars L2b, U1a and U1b. Note different y-axis scales for CH_3Cl .

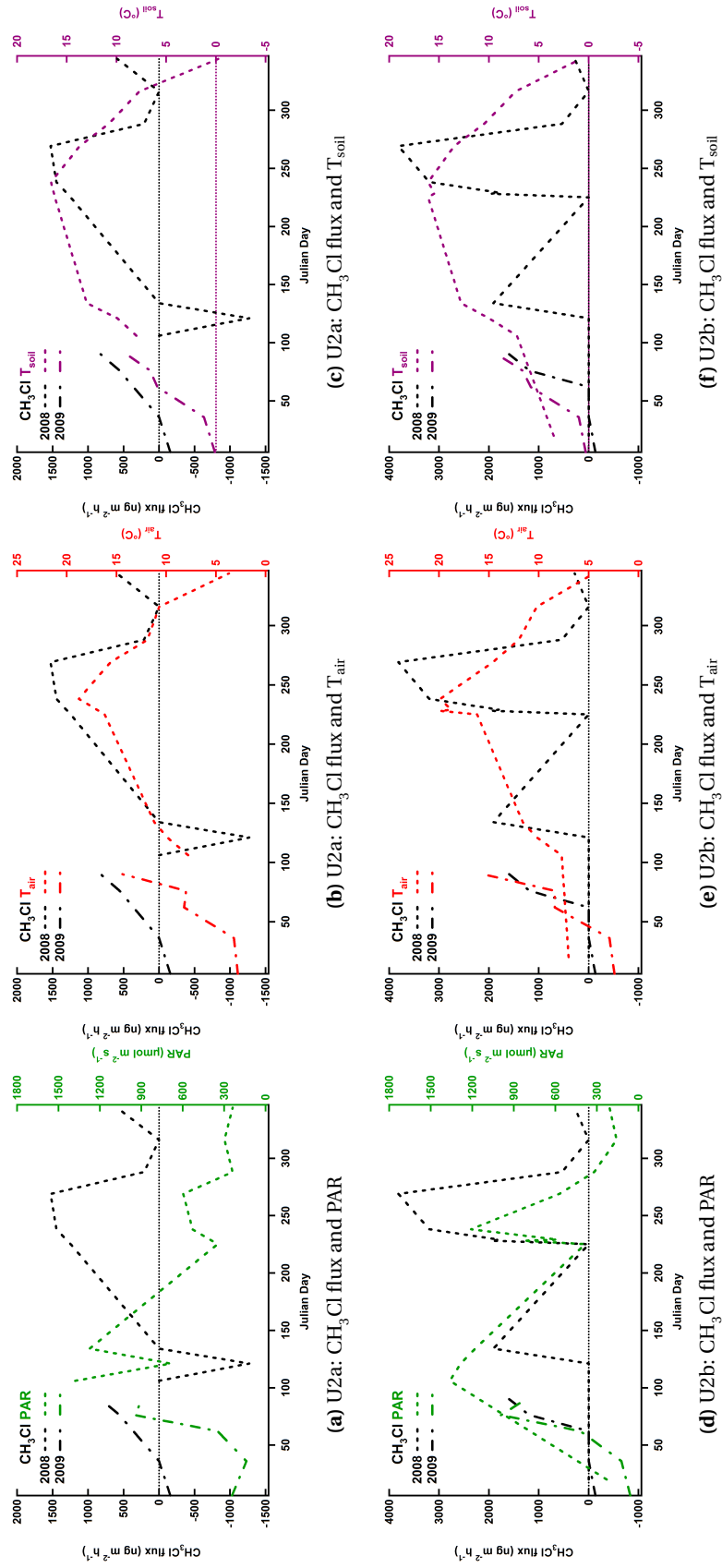


Figure 3.20: Comparison of seasonal net CH_3Cl fluxes with possible drivers at Heckie's Hole for 2008 and 2009 for collars U2a and U2b. Note different y-axis scales for CH_3Cl .

Table 3.7: Mean, median, minimum and maximum net CH₃Cl fluxes at Heckie's Hole for the entire measurement period. All flux values are given as ng m⁻² h⁻¹. The penultimate column shows the coefficient *R* for correlation between CH₃Br and CH₃Cl fluxes. Correlation coefficients which were statistically significant (*P* ≤ 0.05) are in bold. The final column gives the number of measurements.

Collar	Mean	Median	Min	Max	<i>R</i>	number
L1a	483	0	-499	2 644	0.86	14
L1b	1 523	1 454	-201	6 404	0.88	16
L2a	1 477	629	0	5 988	0.87	14
L2b	1 096	99	-145	5 179	0.83	17
U1a	624	332	-1 606	2 962	0.61	13
U1b	585	0	-539	3 538	0.54	18
U2a	383	214	-1 270	1 528	0.53	13
U2b	950	281	-134	3 819	0.78	17
All	904	105	-1 606	6 404	0.61	122

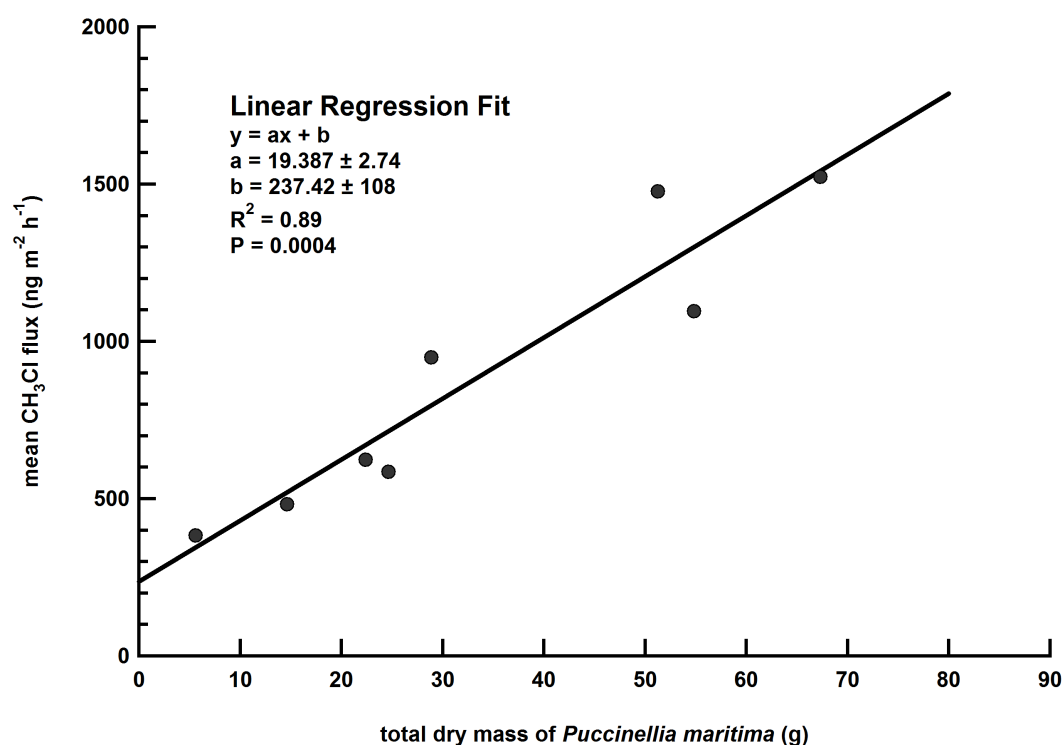


Figure 3.21: Linear relationship between mean CH₃Cl fluxes and total dry mass of *Puccinellia maritima* for collars at Heckie's Hole as determined at the end of the measurement period. Mean CH₃Cl flux values were derived from the entire 2 years of measurements at Heckie's Hole.

- There was no statistically significant correlation ($P < 0.05$) between mean CH_3Cl fluxes and the Cl mass in above-ground vegetation in each collar.

CH_3Br fluxes at Hollands Farm Figures 3.22 to 3.26 show all seasonal CH_3Br fluxes for all 13 collars together with the respective PAR levels, ambient air temperature and soil temperature for the years 2007, 2008 and 2009. From these figures the following observations can be made:

- The seasonal patterns of net CH_3Br fluxes for each collar were often—but not always—similar for the years 2007 and 2008. Especially noticeable is the seasonal maximum in 2007 at the end of August (day 234) to the beginning of September (day 250) which for many collars also occurred at a similar time in 2008 (day 241). Apart from these maxima, fluxes in 2007 and 2008 often remained very stable at a lower level. In 2009 a similar phenomenon as seen at Heckie's Hole occurred in some collars with fluxes rising during early spring to the beginning of April (day 168) to levels equal to the annual maxima seen during 2007. PAR and ambient air and soil temperatures were all elevated at that time compared to spring 2008.
- The two collars of a collar pair often displayed very similar flux patterns and magnitudes, whereas the flux patterns and magnitudes between different collar pairs were much more distinct. This is despite the fact that there were often considerable differences in vegetation make-up for the collars of each collar pair. This may point to hydrological factors, such as differences in percentage of sand or silt in the soil or the relative elevation of a specific location of a collar pair; indeed a statistically significant negative correlation ($R = -0.60$, $P = 0.03$) between relative elevation and mean CH_3Br fluxes shows that lower lying areas of the marsh were associated with higher CH_3Br production.
- As at Heckie's Hole no uptake of CH_3Br was measured. This is especially significant since collar S contained no vegetation and would be expected to uptake CH_3Br during summer when temperatures were high enough for micro-biological activity. Thus soil micro-organisms are either not significant for CH_3Br uptake in general or not abundant/active at Hollands Farm. On the other hand conditions at collar S were probably extremely harsh for soil micro-organisms as the area was regularly inundated with salt water, low in SOM and exposed to solar radiation.
- Minimum fluxes in each collar were in the range of $0\text{--}120\text{ ngm}^{-2}\text{ h}^{-1}$ and maximum fluxes ranged from 140 to $3\,400\text{ ngm}^{-2}\text{ h}^{-1}$ (Table 3.8). The highest mean fluxes were recorded from collar pairs L1 and L3 which were ~ 750 and $\sim 500\text{ ngm}^{-2}\text{ h}^{-1}$,

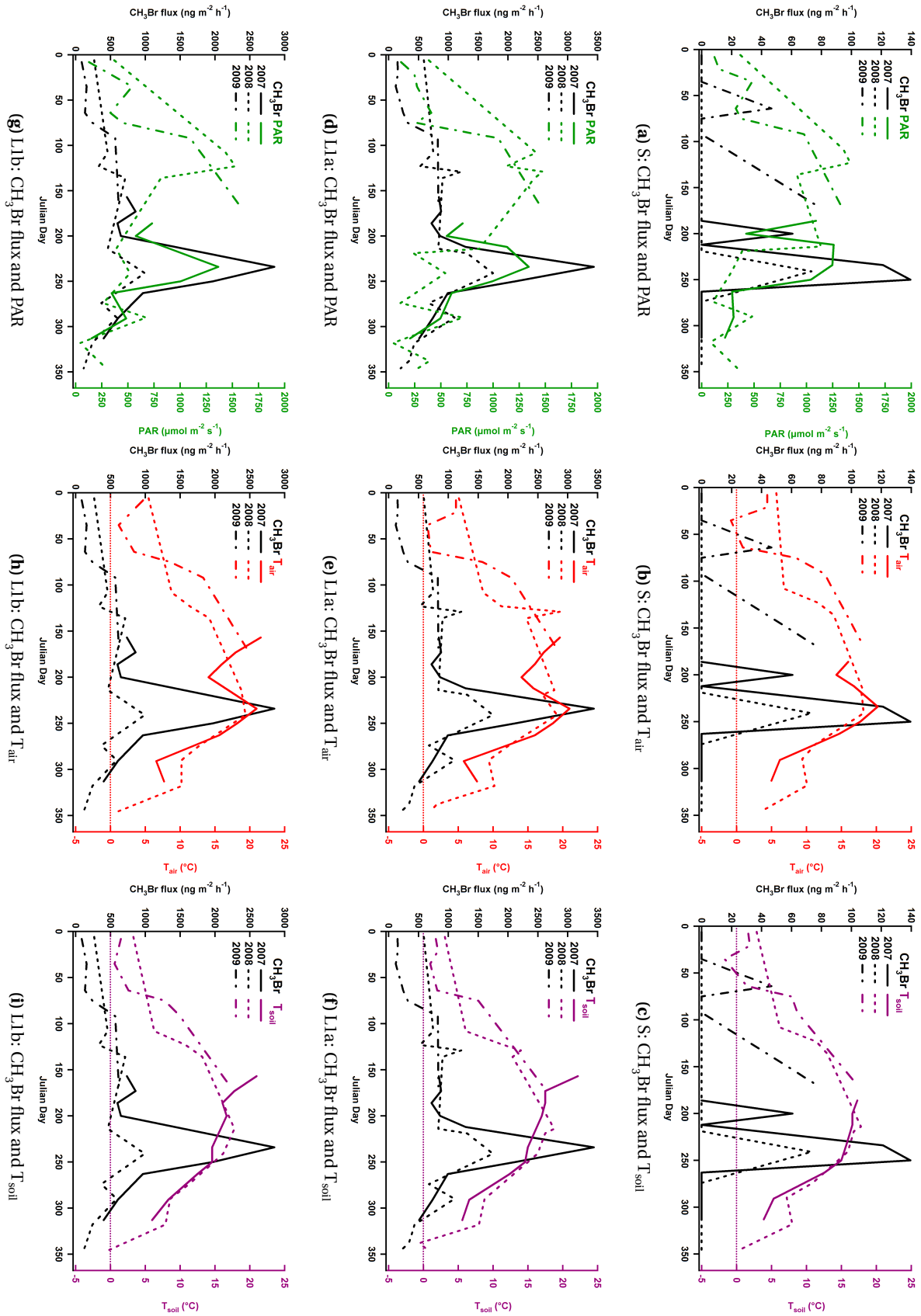


Figure 3.22: Comparison of seasonal net CH_3Br fluxes with possible drivers at Hollands Farm for 2007, 2008 and 2009 for collars S, L1a and L1b. Note different y-axis scales for CH_3Br .

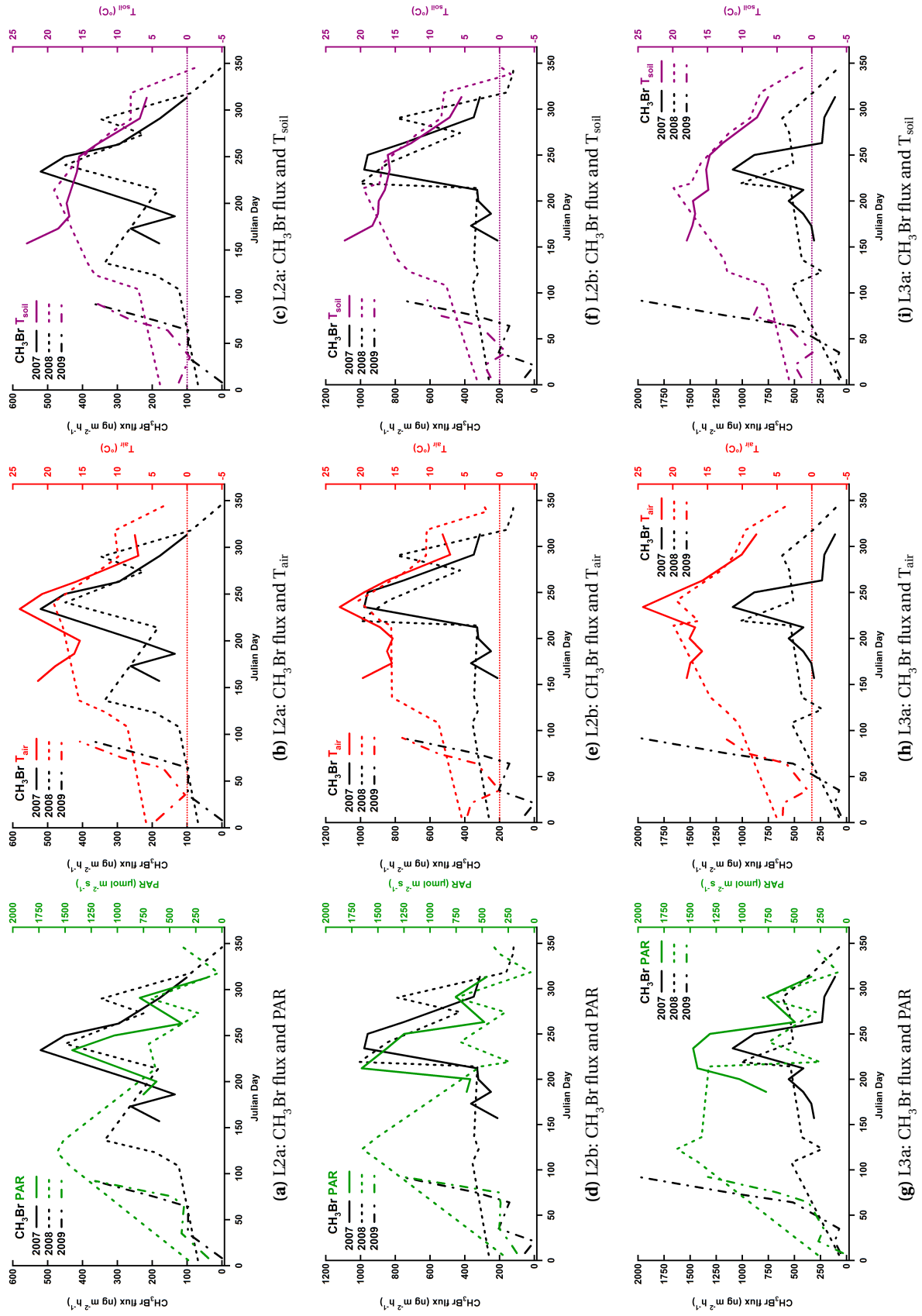


Figure 3.23: Comparison of seasonal net CH_3Br fluxes with possible drivers at Hollands Farm for 2007, 2008 and 2009 for collars L2a, L2b and L3a. Note different y-axis scales for CH_3Br .

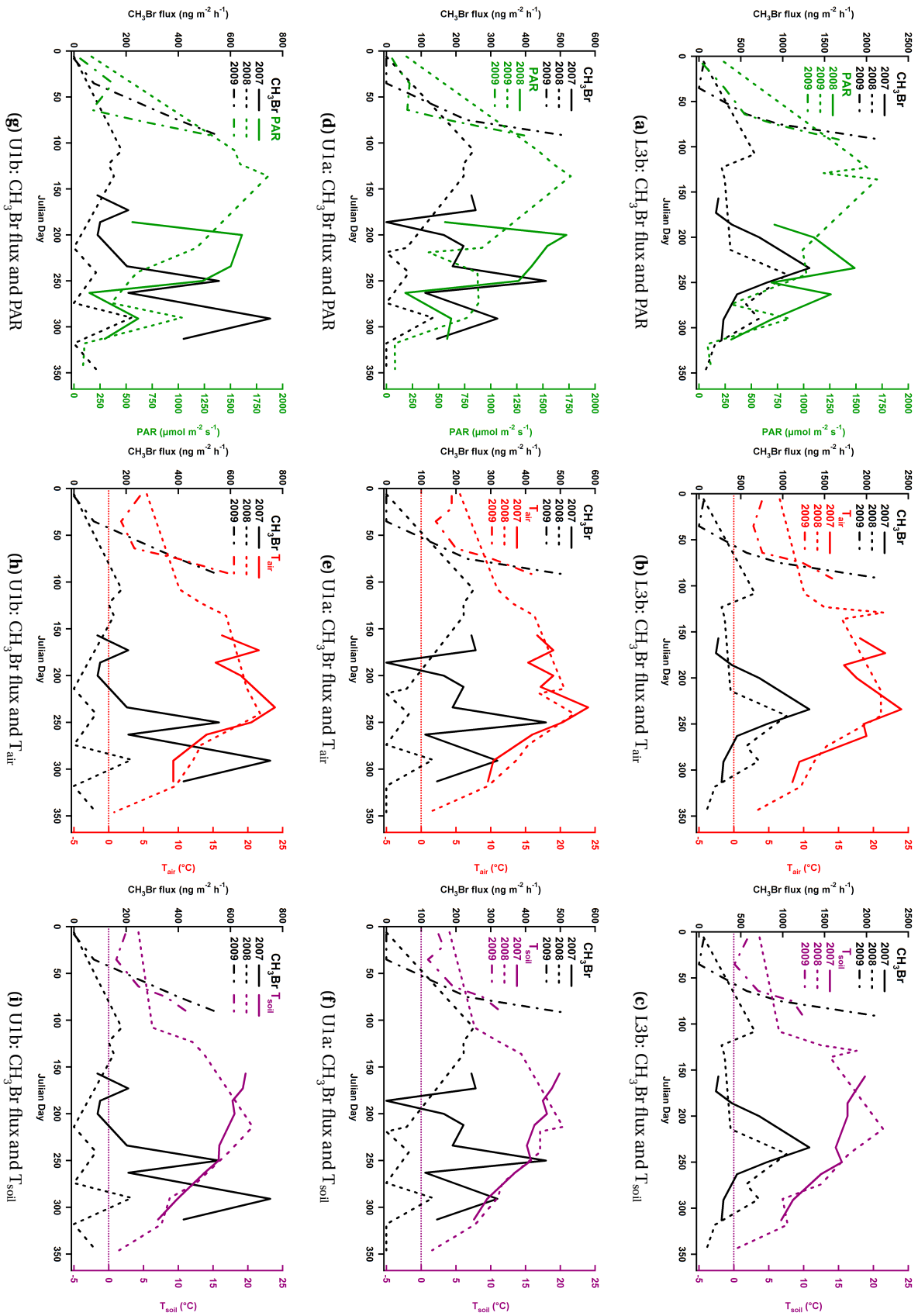


Figure 3.24: Comparison of seasonal net CH_3Br fluxes with possible drivers at Hollands Farm for 2007, 2008 and 2009 for collars L3b, U1a and U1b. Note different y-axis scales for CH_3Br .

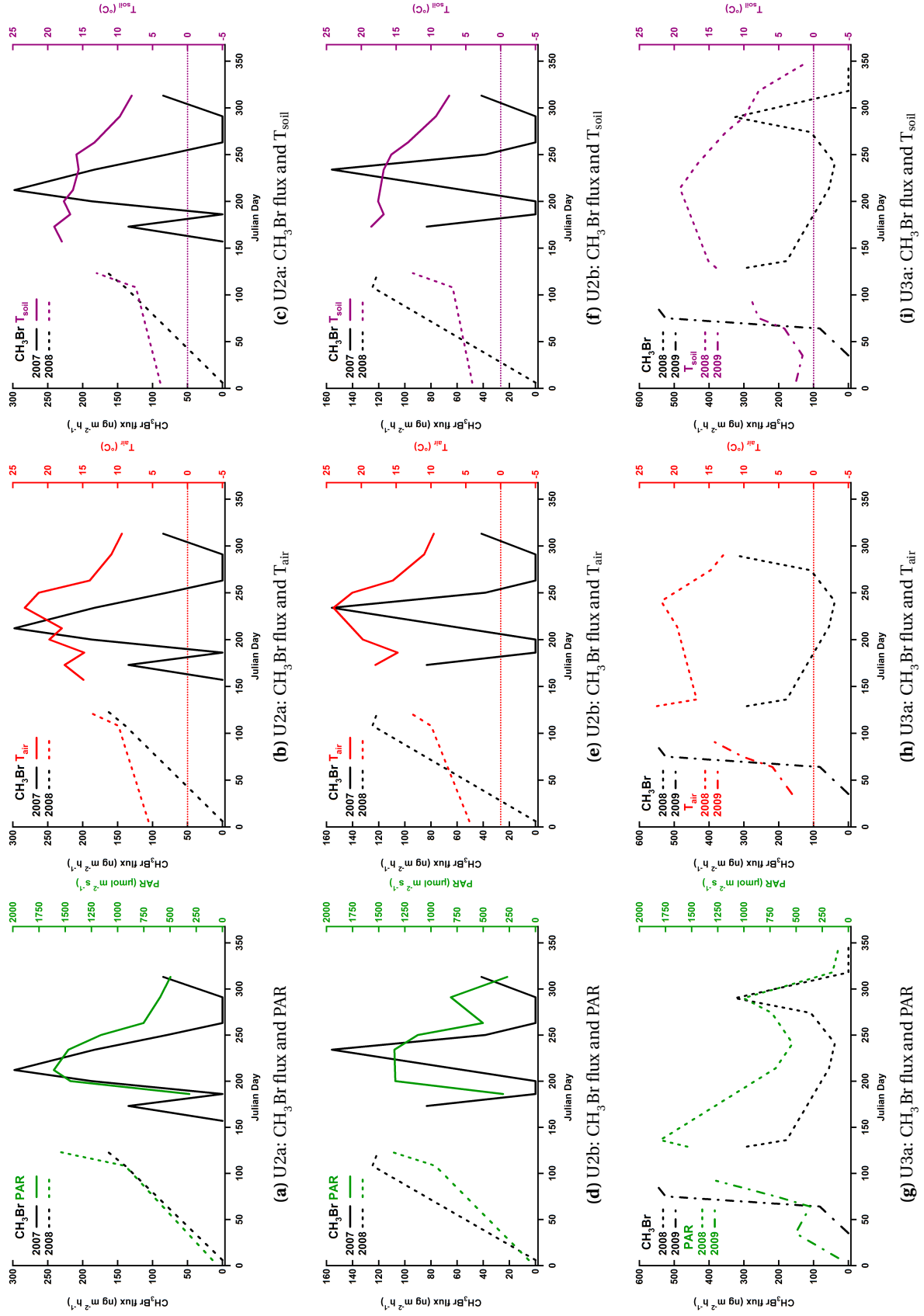


Figure 3.25: Comparison of seasonal net CH₃Br fluxes with possible drivers at Hollands Farm for 2007, 2008 and 2009 for collars U2a, U2b and U3a. Note different y-axis scales for CH₃Br.

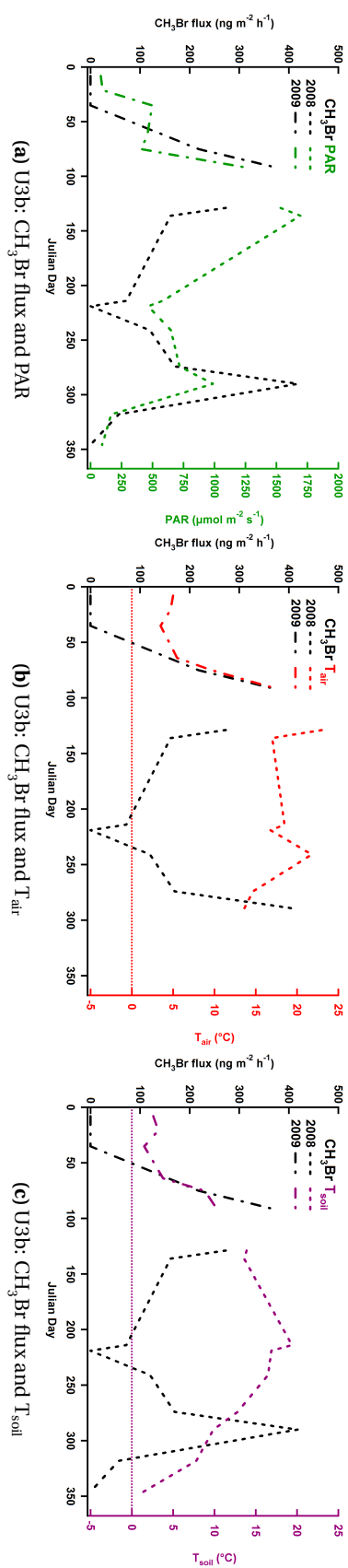


Figure 3.26: Comparison of seasonal net CH_3Br fluxes with possible drivers at Hollands Farm for 2008 and 2009 for collar U3b.

respectively, whilst the average of the remaining collars was less than $400 \text{ ngm}^{-2} \text{ h}^{-1}$. Average fluxes during the growing season were 2.9 times the fluxes in the non-growing season.

Table 3.8: Mean, median, minimum and maximum net CH_3Br fluxes at Hollands Farm for the entire measurement period. All flux values are given as $\text{ngm}^{-2} \text{ h}^{-1}$. The final column gives the number of measurements. The last two rows present all fluxes from collars with vegetation and all collars including collar S respectively.

Collar	Mean	Median	Min	Max	number
S	20	0	0	139	26
L1a	858	788	122	3 440	30
L1b	641	569	89	2 854	25
L2a	214	188	0	521	24
L2b	408	329	0	1 005	28
L3a	495	417	57	1 993	27
L3b	522	377	0	2 174	25
U1a	147	140	0	515	26
U1b	197	132	0	753	23
U2a	98	85	0	298	13
U2b	51	38	0	156	11
U3a	181	95	0	560	12
U3b	133	96	0	418	14
All (excluding S)	383	241	0	3 440	258
All (including S)	350	213	0	3 440	284

- Flux magnitude was neither correlated with the amount of Br measured in the vegetation of a collar nor with vegetation composition.

In summary, net CH_3Br fluxes at Hollands Farm were determined by specific position/relative elevation in the marsh, with greater variation between collar pairs than within collar pairs. No single factor, nor the occurrence of a specific plant species clearly accounted for the apparent differences in flux patterns or magnitude. Maximum fluxes at Hollands Farm were higher than at Heckie's Hole although unweighted average net fluxes for the whole salt marsh were only $350 \text{ ngm}^{-2} \text{ h}^{-1}$ at Hollands Farm and $440 \text{ ngm}^{-2} \text{ h}^{-1}$ at Heckie's Hole. Again there was no measured net uptake of CH_3Br even when vegetation was absent or dormant.

CH_3Cl fluxes at Hollands Farm Figures 3.27 to 3.30 show all seasonal CH_3Cl fluxes for all collars except collar pair U2, together with the respective PAR levels, ambient air temperature and soil temperature for the years 2008 and 2009. From these figures the following observations can be made:

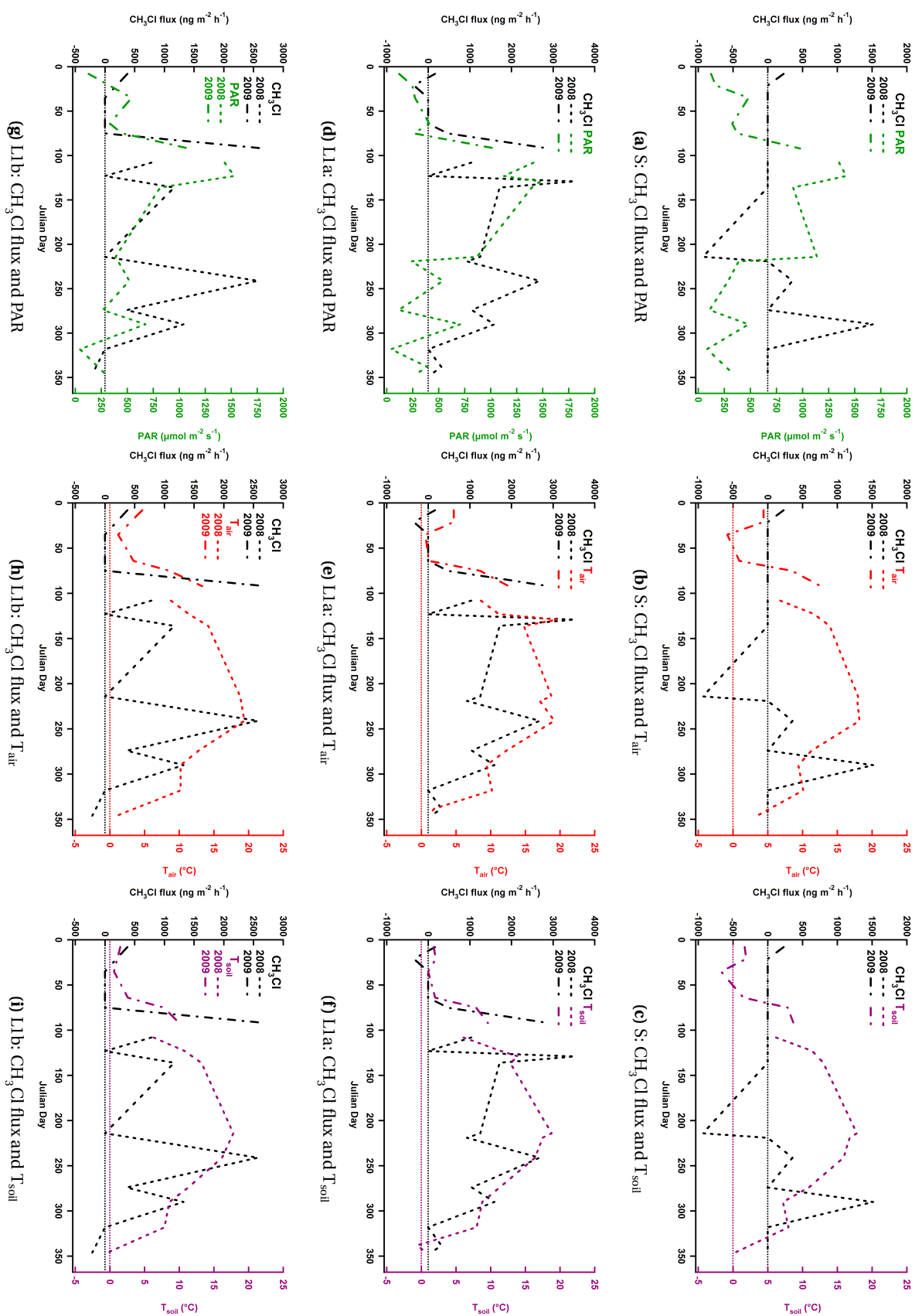


Figure 3.27: Comparison of seasonal net CH_3Cl fluxes with possible drivers at Hollands Farm for 2008 and 2009 for collars S, L1a and L1b. Note different y-axis scales for CH_3Cl .

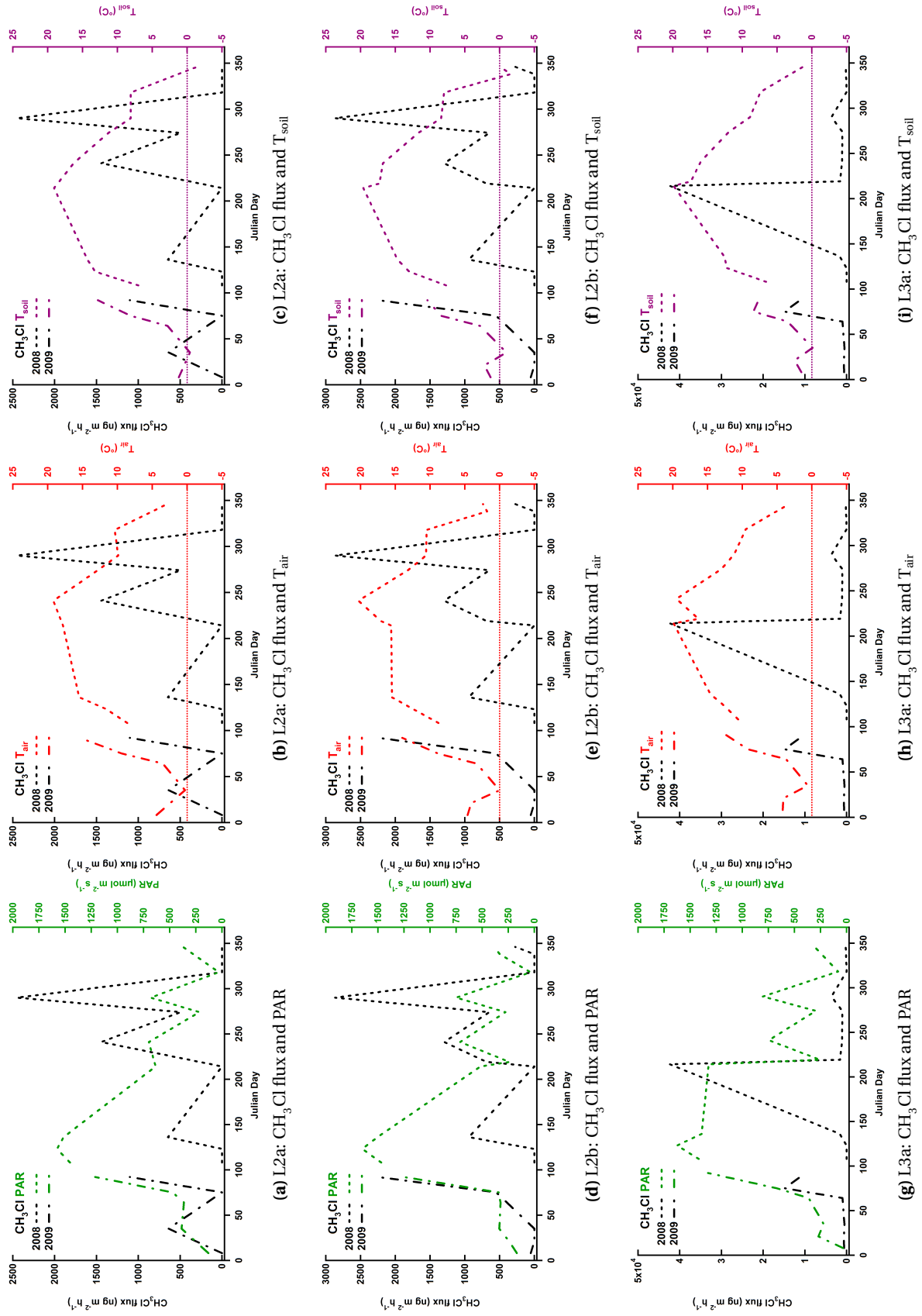


Figure 3.28: Comparison of seasonal net CH_3Cl fluxes with possible drivers at Hollands Farm for 2008 and 2009 for collars L2a, L2b and L3a. Note different y-axis scales for CH_3Cl .

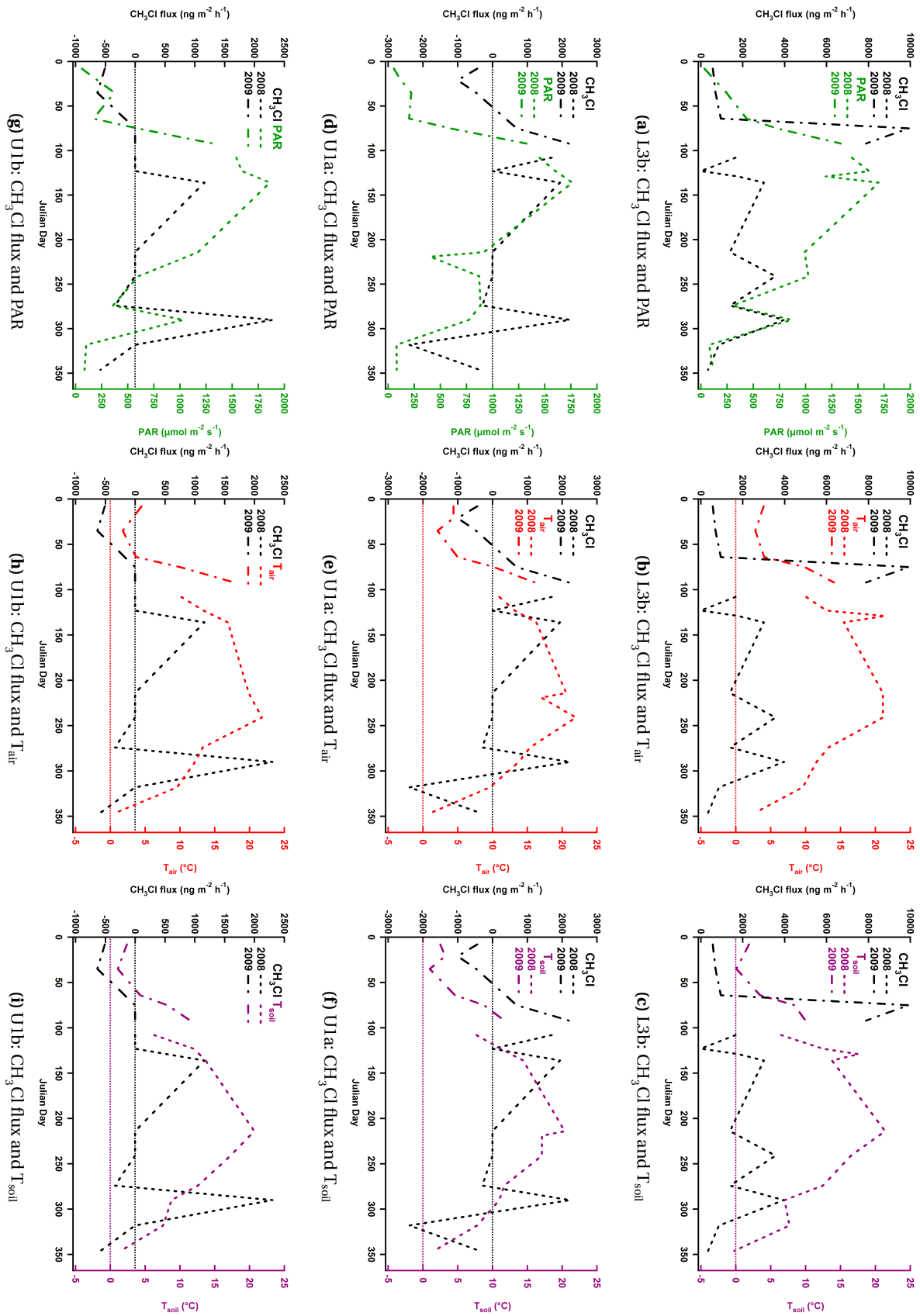


Figure 3.29: Comparison of seasonal net CH_3Cl fluxes with possible drivers at Hollands Farm for 2008 and 2009 for collars L3b, U1a and U1b. Note different y-axis scales for CH_3Cl .

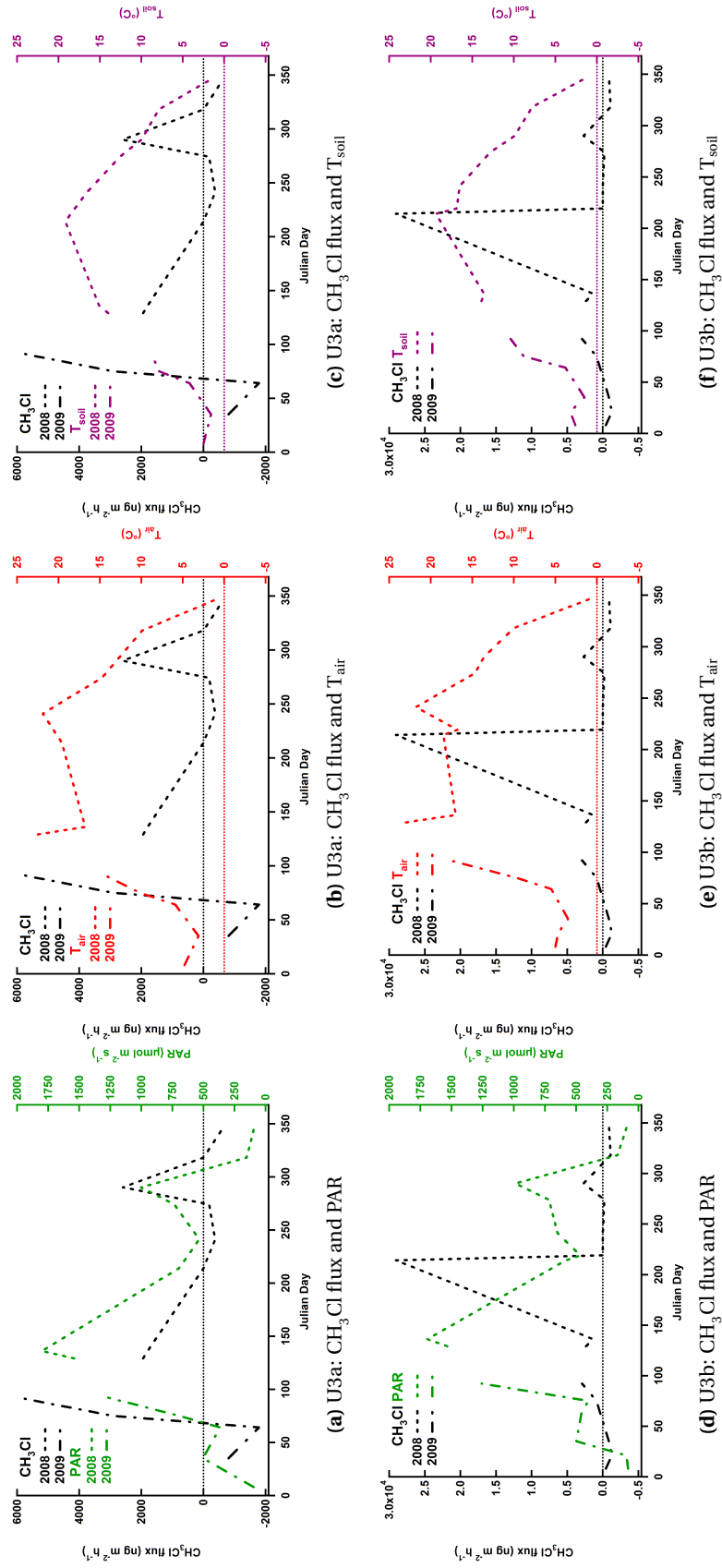


Figure 3.30: Comparison of seasonal net CH_3Cl fluxes with possible drivers at Hollands Farm for 2008 and 2009 for collars U2a, U2b and U3a. Note different y-axis scales for CH_3Cl .

- As at Heckie's Hole, CH₃Cl fluxes at Hollands Farm had similar annual patterns to CH₃Br fluxes but up to one order of magnitude larger amplitudes.
- Flux patterns and magnitude were often similar for the two collars of a collar pair, whilst both differed markedly between different collar pairs.
- CH₃Br and CH₃Cl fluxes were significantly correlated for both collars at L1 and L2 and at collars L3b, U1a and U3a (R range 0.73–0.91 (Table 3.9)). There was no significant correlation between methyl halide fluxes in the other four collars.

Table 3.9: Mean, median, minimum and maximum net CH₃Cl fluxes at Hollands Farm for the entire measurement period. All flux values are given as ngm⁻²h⁻¹. The penultimate column shows the coefficient R for correlation between CH₃Br and CH₃Cl fluxes ($P < 0.05$). Statistically significant correlation coefficients are in bold. The final column gives the number of measurements. The last two rows present all fluxes from collars with vegetation and all collars including collar S, respectively.

Collar	Mean	Median	Min	Max	R	number
S	78	0	−933	1 514	0.16	15
L1a	964	702	−344	3 518	0.80	18
L1b	648	185	−211	2 696	0.82	14
L2a	521	0	0	2 450	0.73	13
L2b	598	165	0	2 868	0.73	16
L3a	4 946	1 037	0	42 343	0.28	16
L3b	2 536	1 399	0	9 929	0.77	15
U1a	254	0	−2 385	2 222	0.75	15
U1b	108	0	−632	2 301	0.24	13
U3a	952	0	−1 783	5 938	0.91	12
U3b	2 479	0	−1 262	29 048	0.05	14
All (excluding S)	1 447	361	−2 385	42 343	0.31	146
All (including S)	1 320	163	−2 385	42 343	0.32	161

- Maximum, minimum and mean net fluxes for individual collars were in the ranges 1 500–42 000 ngm⁻²h⁻¹, −2 400–0 ngm⁻²h⁻¹ and 78–4 900 ngm⁻²h⁻¹, respectively. The highest fluxes were recorded from collar pairs L3 and U3 whilst the lowest fluxes were measured for U1 (except collar S which had no vegetation). If CH₃Cl uptake occurred it was towards the end of the growing season and during the non-growing season, whilst flux maxima could occur at any time during the year.
- Mean seasonal net CH₃Cl fluxes were positively correlated with total dry mass of *Aster tripolium* ($R = 0.85$, $P = 0.002$), *Juncus gerardi* ($R = 0.65$, $P = 0.04$) and *Plantago maritima* ($R = 0.84$, $P = 0.003$) but negatively correlated with total dry mass of

Puccinellia maritima ($R = -0.87$, $P = 0.001$) in individual collars. Furthermore total dry mass of *Aster tripolium* and *Plantago maritima* were negatively correlated with *Puccinellia maritima* ($P < 0.05$, $R = -0.70$ and -0.83 respectively). This is in direct contrast to the measurements at Heckie's Hole where mean CH_3Cl fluxes were positively correlated with total dry mass of *Puccinellia maritima* in individual collars. This suggests that CH_3Cl flux magnitudes at individual sites depend on the abundance of specific species and that *Puccinellia maritima* was the strongest emitter of CH_3Cl at Heckie's Hole whilst it was a weak emitter of CH_3Cl at Hollands Farm in comparison with the stronger emissions from the above-mentioned species also present in a number of collars.

- Since the time periods for measurements in years 2008 and 2009 do not overlap it is difficult to make inter-annual comparisons. However, fluxes at the beginning of 2009 were often very high for the time of year considering that plants, which are seen as the main producers of methyl halides, had either not yet started regrowth or were in the early stages of growth.

Overall the findings for CH_3Cl fluxes are different to CH_3Br fluxes at Hollands Farm. CH_3Cl fluxes from a collar appeared to be mainly determined by total dry mass of *Aster tripolium*, *Juncus gerardi* and *Plantago maritima*. Maximum CH_3Cl fluxes were substantially higher at Hollands Farm than at Heckie's Hole. Total unweighted average fluxes at Hollands Farm were $1300 \text{ ng m}^{-2} \text{ h}^{-1}$ compared to $900 \text{ ng m}^{-2} \text{ h}^{-1}$ at Heckie's Hole. One possible explanation for the apparent difference in CH_3Cl emissions between the two sites is that plants present at Hollands Farm (*Aster tripolium* at collars L1a, L3a and L3b, *Juncus gerardi* at collars L3a, U1a and U1b, *Triglochin maritima* at collars L3b and U3b) were absent or were not a major part of the vegetation mixture at Heckie's Hole. It also highlights the danger of extrapolation from single site measurements to regional or even global flux estimates.

Summary Methyl halide fluxes at Heckie's Hole generally followed a uniform pattern whereas at Hollands Farm flux patterns within the marsh followed more distinct seasonal trends. The same is true for net flux magnitudes. Whereas fluxes at Heckie's Hole differed between the upper and lower marsh, at Hollands Farm fluxes from the two collars of a pair were often similar but very different to other collar pairs. At Heckie's Hole the magnitude of CH_3Cl fluxes was largely explained by the total dry mass of *Puccinellia maritima* in a specific collar. However, at Hollands Farm the best predictors for CH_3Br and CH_3Cl flux magnitudes were relative elevation and total dry mass of *Aster tripolium*, *Juncus gerardi* and *Plantago maritima*, respectively. It should be remembered that vegetation composition and abundance itself strongly depend on the relative elevation inside a marsh and therefore all of

these factors are ultimately interlinked. CH_3Br fluxes at Heckie's Hole were not significantly correlated to any of the examined factors at a significance level of $P < 0.05$. Average unweighted daytime CH_3Br and CH_3Cl fluxes at Heckie's Hole were 440 and $900 \text{ ng m}^{-2} \text{ h}^{-1}$, respectively, whilst at Hollands Farm average CH_3Br and CH_3Cl fluxes were $350 \text{ ng m}^{-2} \text{ h}^{-1}$ and $1300 \text{ ng m}^{-2} \text{ h}^{-1}$, respectively. Despite the differences between and within the two salt marsh sites the overall flux magnitudes for CH_3Br and CH_3Cl are comparable at Heckie's Hole and Hollands Farm. Flux magnitudes were found to be quite distinct from reported fluxes at salt marshes in China or Southern California. It therefore seems reasonable to treat both sites as one class of "temperate salt marshes", i.e. to assume that methyl halide fluxes from both sites behave overall similarly and are controlled by similar factors even though they are not entirely understood.

3.4.3.2 Statistical analysis of seasonal fluxes and their potential drivers

Statistical analyses were performed in two different ways:

1. Net methyl halide fluxes were analysed for significant differences in flux magnitudes between the two measurement sites, between the growing and non-growing season and between the collars within a site employing the General Linear Model (multi-variate ANOVA) within the Minitab® software package.
2. Normalised methyl halide fluxes within the two sites for the growing season and non-growing season were analysed for their dependency on the measured environmental factors (PAR, ambient air temperature, soil temperature, internal chamber temperature, water table height and soil water content).

For both these procedures the fluxes from collar S and collar pair U2 at Hollands Farm were excluded since the former did not contain any vegetation whilst the latter did not contain vegetation typical of a salt marsh.

Treatment

1. For the analyses of differences between individual collars, the two measurement sites and growing and non-growing season, the raw net flux data from the two sites were tagged according to collar, site and season, where the factor "collar" was nested within the factor "site". Alongside testing of the significance of these factors, it was also tested whether or not there was a significant interaction between season and site. No other data modifications were performed. Two data sets, one for CH_3Br and one for CH_3Cl , were derived.

2. For the analyses of significance of effect of potential drivers on net fluxes over time the following modifications were made to the raw data: (a) Net methyl halide fluxes from an individual collar were normalised against the highest flux of that collar for the whole of the 2 yr-measurement period; (b) Numerical data of PAR, ambient air temperature, soil temperature and internal chamber temperature were left unchanged whereas data of soil water content and water table depth were adjusted for spatial variations within a salt marsh site by subtracting the lowest value measured at each collar from the raw data for that collar; (c) The data so derived from the individual collars were pooled together for each salt marsh site and season to allow for analysis of common factors affecting flux variations over time;
3. All testing was performed to a 95 % significance level. Whilst this was straightforward for the ANOVA method the results from the regression analysis of temporal flux changes had to account for the statistical effect of multiple testing. For this purpose a Bonferroni correction [Abdi, 2007] was applied. This correction method accounts for the higher chance of a “Type I” error due to a higher number of tests by lowering the critical significance level of the individual tests performed.

Results of ANOVA Analysis of variations according to site, season and collar revealed that there was no significant differences in flux magnitudes between the two salt marsh sites for either CH_3Br or CH_3Cl (Table 3.10). However there was a significant difference in flux magnitudes between season and between collars at a site for both methyl halides. This indicates that there is a greater variability in net fluxes within a salt marsh than there is between the two salt marsh sites. It also affirms the correctness of separating the year into these two different seasons. There was no significant interaction between season and site.

Table 3.10: *F* and *P* values for the effect of season, site and collar on methyl halide flux magnitudes as derived by multi-variate ANOVA. Also shown are the corresponding values for the season-site interaction terms and the degrees of freedom (d.f.).

Factor	CH_3Br			CH_3Cl		
	d.f.	<i>F</i>	<i>P</i>	d.f.	<i>F</i>	<i>P</i>
Season	1	148.50	<0.001	1	13.06	<0.001
Site	1	0.11	0.746	1	1.27	0.262
Season*Site	1	1.32	0.251	1	0.49	0.483
Collar	16	10.83	<0.001	16	1.82	0.029
Residual	429			244		

The analysis of temporal flux variations and their dependency on drivers such as temperature and light yielded very interesting results (Table 3.11). Net CH_3Br and CH_3Cl fluxes from

collars at Heckie's Hole during the growing season varied significantly with ambient air, internal chamber and soil temperature at 10 cm depth. At Hollands Farm there was only a weak correlation between net flux variations of CH_3Br and internal chamber temperature. However, there was no significant influence of PAR on net methyl halide fluxes from either salt marsh site. This lack of correlation is surprising since it has been widely suggested that sunlight levels are the most important drivers for methyl halide production by plants [Dimmer et al., 2001; Manley et al., 2006; Wang et al., 2006; Drewer et al., 2006]. Instead the findings from this study suggest that at the study sites the main process of methyl halide production from plants could be as secondary metabolites in plants. This S-adenosyl-L-methionine (SAM) methyl transferase dependent reaction [Manley, 2002; Attieh et al., 1995] is light independent since it is not directly coupled to the primary metabolic pathway of photosynthesis. Instead a temperature dependency of the enzyme activity and therefore of the methyl halide production rate would be expected.

Table 3.11: Individual Pearson product-moment correlation coefficients R between potential drivers and methyl halide fluxes during the growing and non growing season at Heckie's Hole (HH) and Hollands Farm (HF). Soil water content and water table height are denoted wc and wt, respectively. R values printed bold indicate a statistically significant correlation equivalent to $P \leq 0.05$. To calculate the individual significance levels a Bonferroni correction at $n = 48$ was applied.

Factor	Growing Season				Non-growing Season			
	CH_3Br		CH_3Cl		CH_3Br		CH_3Cl	
	HH	HF	HH	HF	HH	HF	HH	HF
PAR	0.17	0.16	-0.20	0.06	0.59	0.63	0.72	0.49
T_{air}	0.53	0.14	0.52	-0.05	0.83	0.49	0.35	0.19
T_{chamber}	0.54	0.34	0.41	0.13	0.83	0.55	0.66	0.30
T_{soil}	0.53	-0.16	0.43	-0.15	0.85	0.53	0.41	0.17
wc	-0.04	0.01	-0.16	-0.14	0.09	0.05	0.06	0.19
wt	0.01	0.00	-0.18	0.13	0.05	-0.06	0.07	0.33

During the non-growing season net CH_3Br fluxes at the two sites varied significantly with both PAR and all three measures of temperature. Again this is surprising since, by the here used definition of non-growing season, there is no living plant material to react to changes in sunlight levels. However, it could be possible that sunlight levels indirectly influenced CH_3Br production by the soil-microbial community by raising soil temperatures. For CH_3Cl fluxes there was a significant correlation between net fluxes and PAR levels, however of the different measures of temperature only CH_3Cl fluxes at Heckie's Hole showed a significant correlation to internal chamber temperatures.

There was no significant correlation between soil water content or water table depth and net methyl halide fluxes for either site and season. Also, the correlation coefficients that were

found to be statistically significant were in general weaker for the growing season than during the non-growing season. This finding might be explained by the inherent variations in the response to the various drivers during the growing season when plants undergo the different stages of their life-cycle whilst this variation will be absent during the non-growing season.

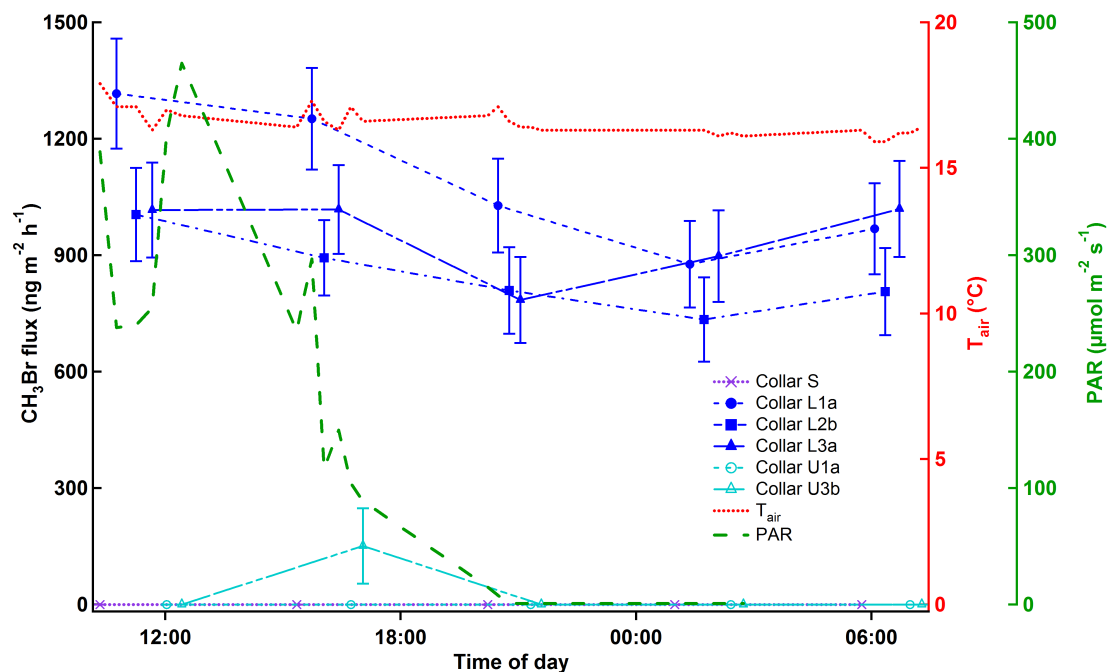
Overall net methyl halide fluxes at Heckie's Hole were more strongly correlated with the examined drivers than net fluxes at Hollands Farm. Temperature was found to be the best predictor of daytime methyl halide fluxes at both sites during the growing season when most of the methyl halides are produced. However, during the non-growing season light levels were equally good predictors. Despite these trends, the data do not allow for a precise prediction of temporal flux changes and correlation coefficients were often low ($R \leq 0.6$).

3.4.4 Diurnal fluxes

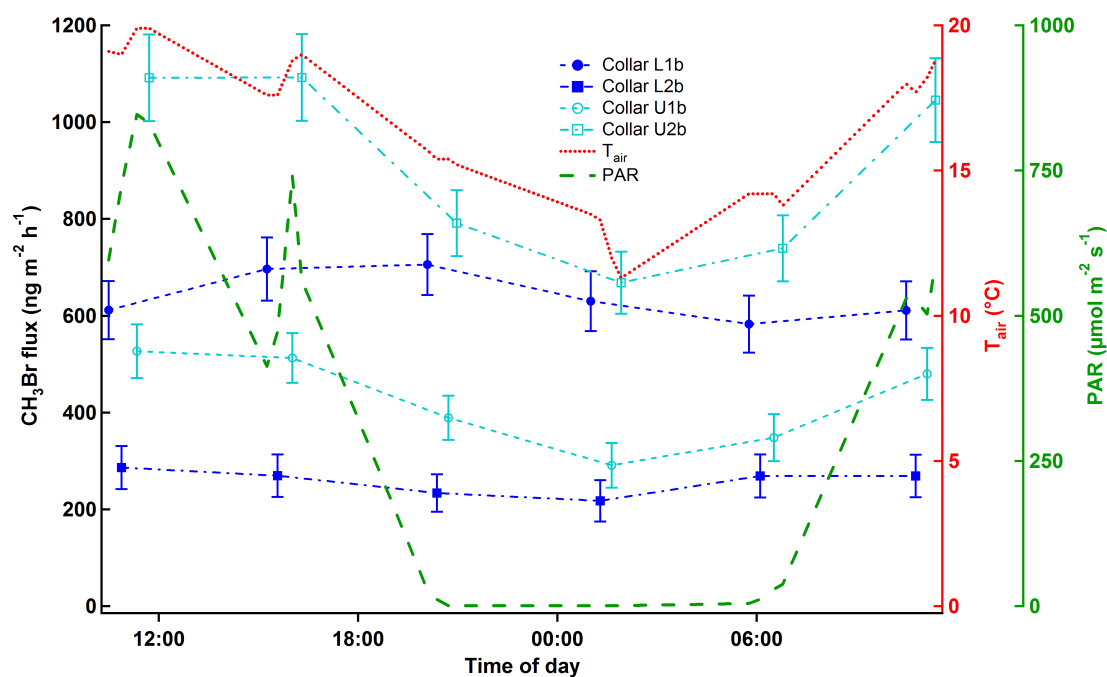
Diurnal studies were conducted twice in summer (8th–9th August 2007 and 15th–16th August 2008 at Heckie's Hole and 31st July–1st August 2007 and 6th–7th August 2008 at Hollands Farm) and once in winter (20th–21st January 2008 at Heckie's Hole and 21st January 2009 at Hollands Farm) for each salt marsh resulting in 6 datasets for CH₃Br and four datasets for CH₃Cl (there are no CH₃Cl flux data for 2007). Only 8 of the 10 diurnal studies are shown here (Figures 3.31 to 3.34) but similar results were observed in all the studies conducted.

CH₃Br Although variations in net fluxes were often small, summertime CH₃Br fluxes at Hollands Farm frequently followed a diurnal pattern with smaller fluxes during the night (Figure 3.31a). Fluxes from the 3 vegetated lower marsh collars were always above zero and only fluxes in collar S and the upper marsh collars dropped to zero. There was no general correlation of fluxes with either PAR or ambient air temperature. At Heckie's Hole in summer CH₃Br was emitted from all collars at all times and never dropped to zero (Figure 3.31b). A diurnal trend with higher fluxes during daytime and lower fluxes during night-time was observed. There was no correlation with PAR levels but fluxes sometimes followed the diurnal temperature pattern.

In winter at Hollands Farm, no flux was recorded for either collar S nor for any collars in the upper marsh but CH₃Br fluxes were always measured at L1a and L3a (Figure 3.32a). Emissions from these two collars also followed a diurnal pattern with highest emissions during daytime, following the diurnal temperature trend. There were no correlations between fluxes and PAR levels. Diurnal CH₃Br fluxes at Heckie's Hole in winter were always below 80 ng m⁻² h⁻¹ (Figure 3.32b) and did not follow any pattern nor were there any relationships with either



(a) Hollands Farm 6th–7th August 2008.



(b) Heckie's Hole 15th–16th August 2008.

Figure 3.31: Diurnal CH_3Br fluxes at Hollands Farm and Heckie's Hole in summer plotted against ambient air temperature and PAR. Whiskers incorporate both analytical and sampling uncertainties. Note the different scales in the two figures.

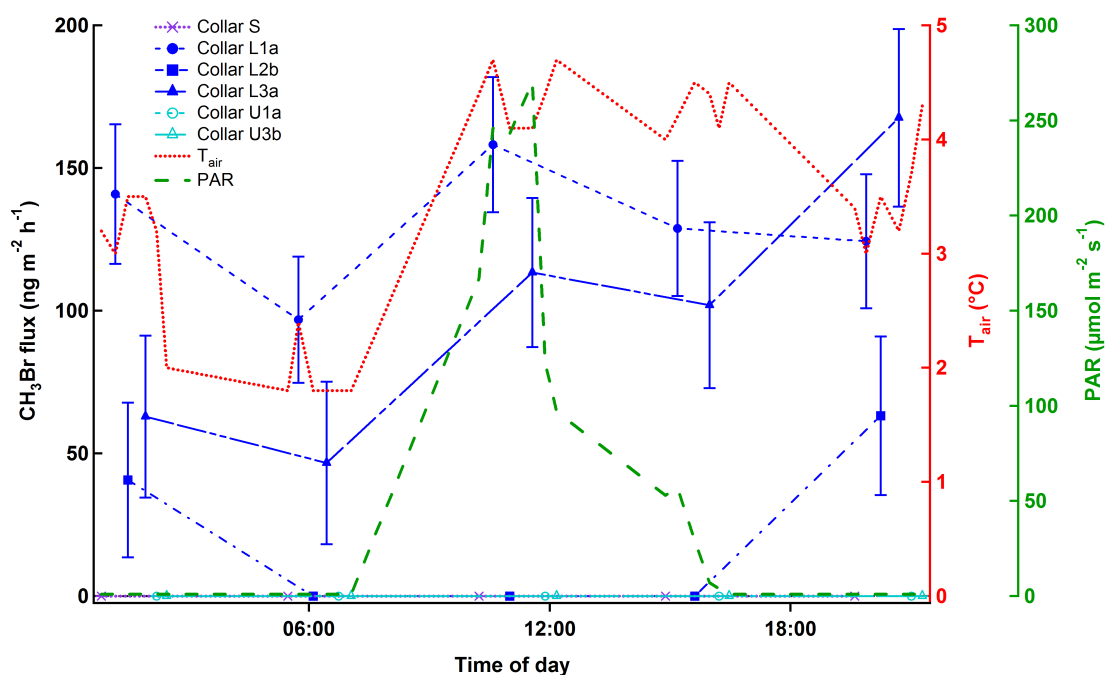
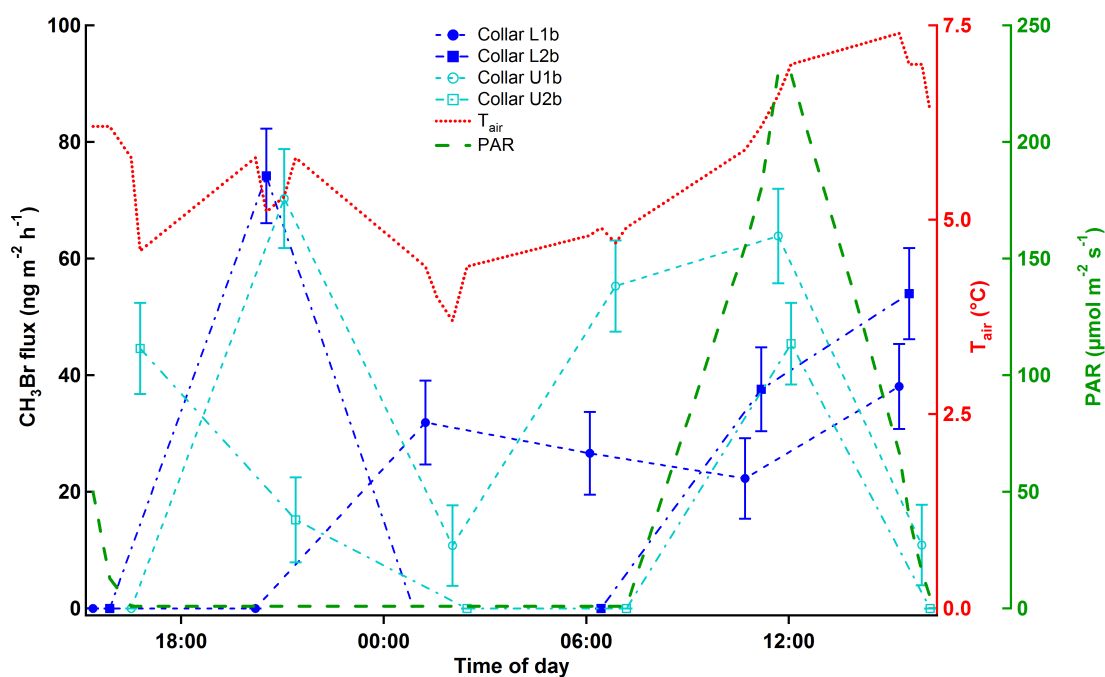
(a) Hollands Farm 21st January 2009.(b) Heckie's Hole 20th–21st January 2008.

Figure 3.32: Diurnal CH_3Br fluxes at Hollands Farm and Heckie's Hole in winter plotted against ambient air temperature and PAR. Whiskers incorporate both analytical and sampling uncertainties. Note the different scales in the two figures.

ambient air temperature nor PAR. CH_3Br fluxes were measured from all collars at some stage during the measurement period. The findings of this study overall agree with those reported by Drewer [2007] for Heckie's Hole, who also observed stronger diurnal net fluxes during summer compared to winter and reported that CH_3Br fluxes did not cease during the night.

CH_3Cl Net CH_3Cl fluxes in summer at both salt marshes were either zero or positive, i.e. no uptake of CH_3Cl was recorded (Figure 3.33). The highest fluxes occurred during daylight hours and often exhibited a diurnal trend. At Hollands Farm the pattern was independent of PAR since fluxes remained high after sunset. However all fluxes (except for collar L1a) declined to zero around midnight and then increased again the following morning (~6:00 -7:00 am). At Heckie's Hole non-zero fluxes coincided with daylight hours but at night all fluxes were zero. Ambient air temperature at Hollands Farm during the summer diurnal study was always 16–18 °C and could not account for the diurnal pattern, whilst temperatures at Heckie's Hole varied between 20 °C during the day and 11 °C at night. However, it seems more likely that the more pronounced changes in PAR levels caused the observed variations in CH_3Cl emissions. During winter CH_3Cl fluxes did not follow any discernible diurnal pattern, and were not correlated with either PAR or temperature (Figure 3.34). All net fluxes at Heckie's Hole were either zero or negative. At Hollands Farm, there was no measured uptake or emissions of CH_3Cl at collar S during the winter diurnal study, whilst fluxes in the lower marsh were either zero or positive, and fluxes in the upper marsh either zero or negative.

Summary Overall net methyl halide fluxes generally followed a diurnal trend in summer but not in winter. Salt marshes did not take up CH_3Br , in either summer or winter, but acted as net sinks for CH_3Cl in winter. In summer CH_3Br fluxes often decreased at night but seldom to zero. In contrast, summertime CH_3Cl emissions from all but one collar in both salt marshes ceased during night time. No general relationship between methyl halide fluxes and either PAR or ambient air temperature was found.

3.4.5 Shading experiment

The shading experiment was conducted on the 31st May 2009 at Heckie's Hole. Ambient air temperature and internal chamber temperature varied between the different shading stages for any particular collar by no more than 3–8 °C. As shown in Figure 3.35, PAR levels did not influence net CH_3Br fluxes.

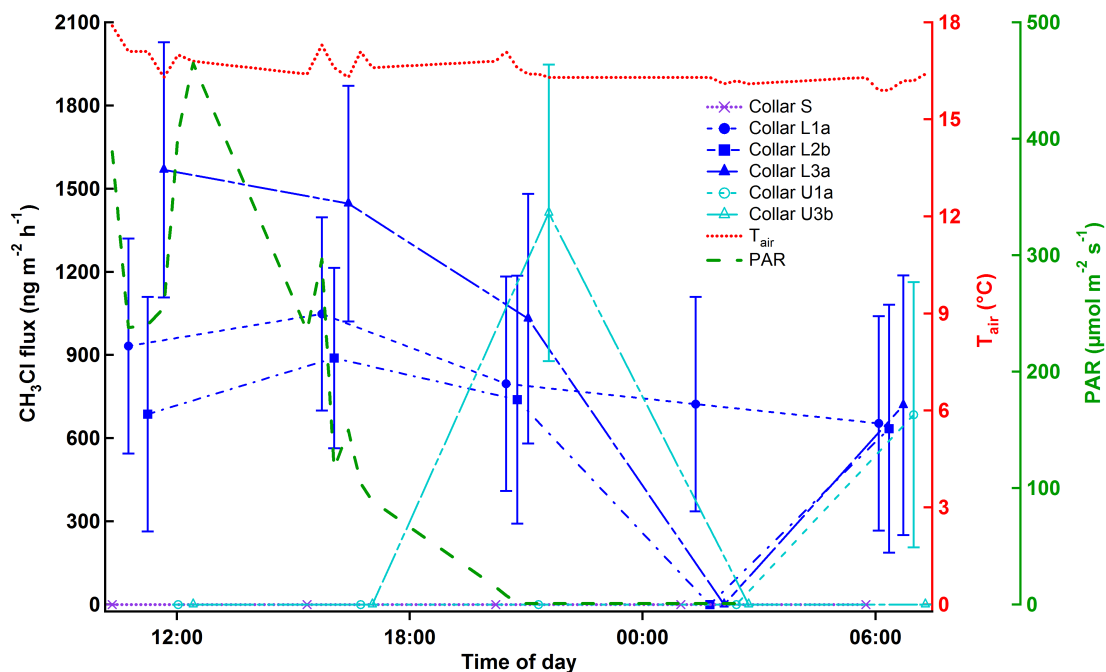
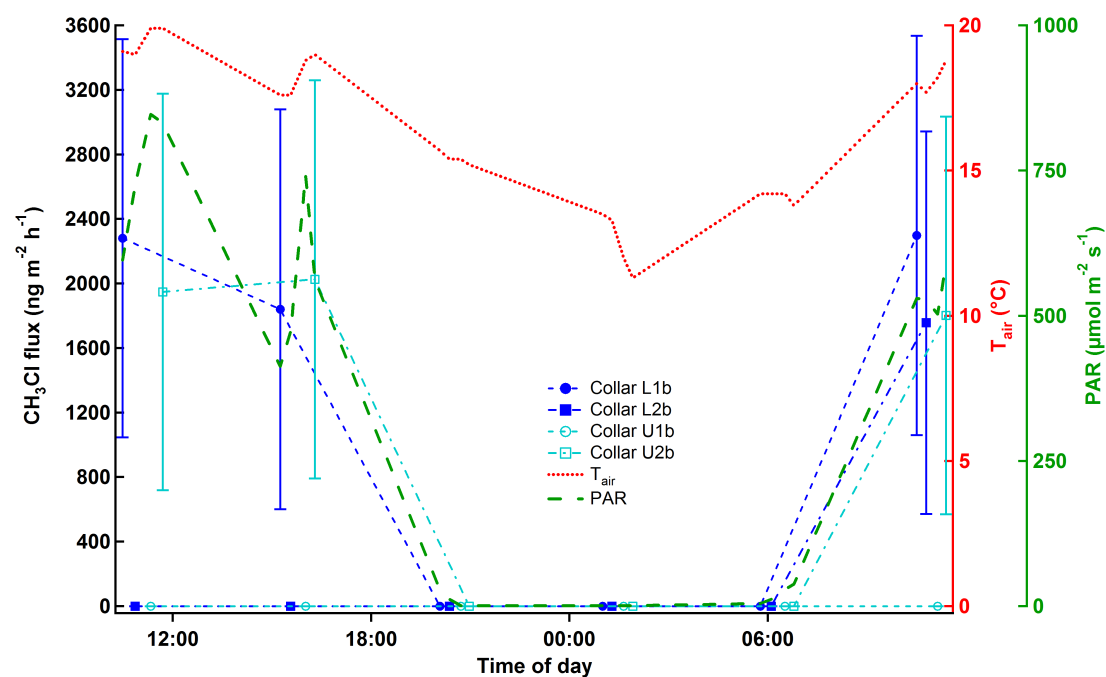
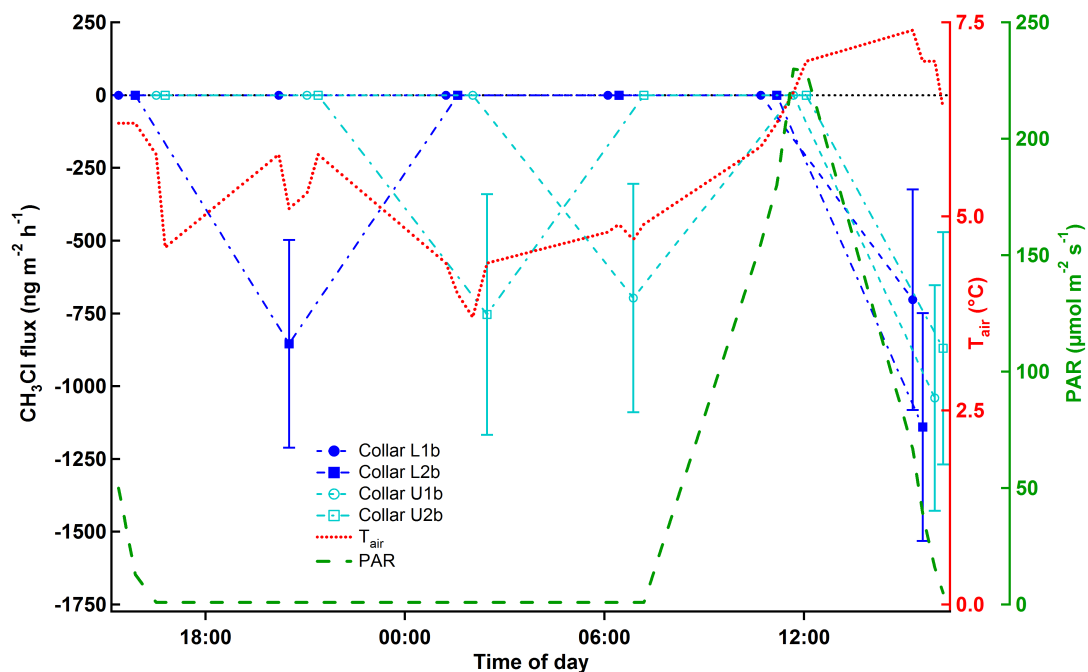
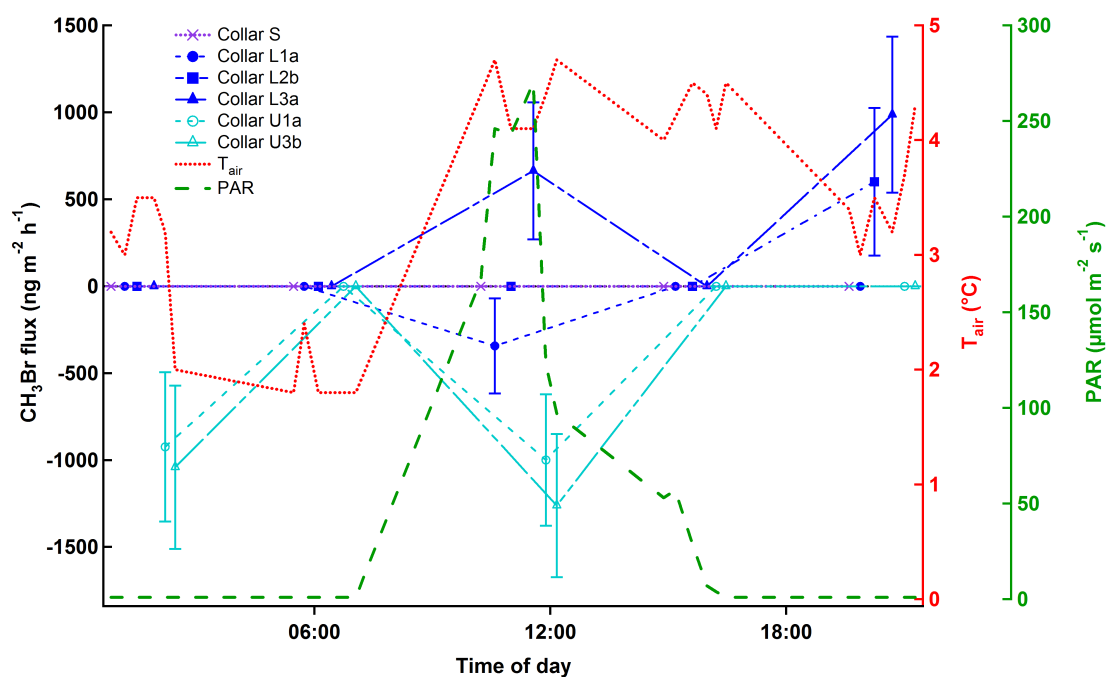
(a) Hollands Farm 6th–7th August 2008.(b) Heckie's Hole 15th–16th August 2008.

Figure 3.33: Diurnal CH_3Cl fluxes at Hollands Farm and Heckie's Hole in summer plotted against ambient air temperature and PAR. Whiskers incorporate both analytical and sampling uncertainties. Note the different scales in the two figures.



(a) Heckie's Hole 20th–21st January 2008.



(b) Hollands Farm 21st January 2009.

Figure 3.34: Diurnal CH_3Cl fluxes at Hollands Farm and Heckie's Hole in winter plotted against ambient air temperature and PAR. Whiskers incorporate both analytical and sampling uncertainties. Note the different scales in the two figures.

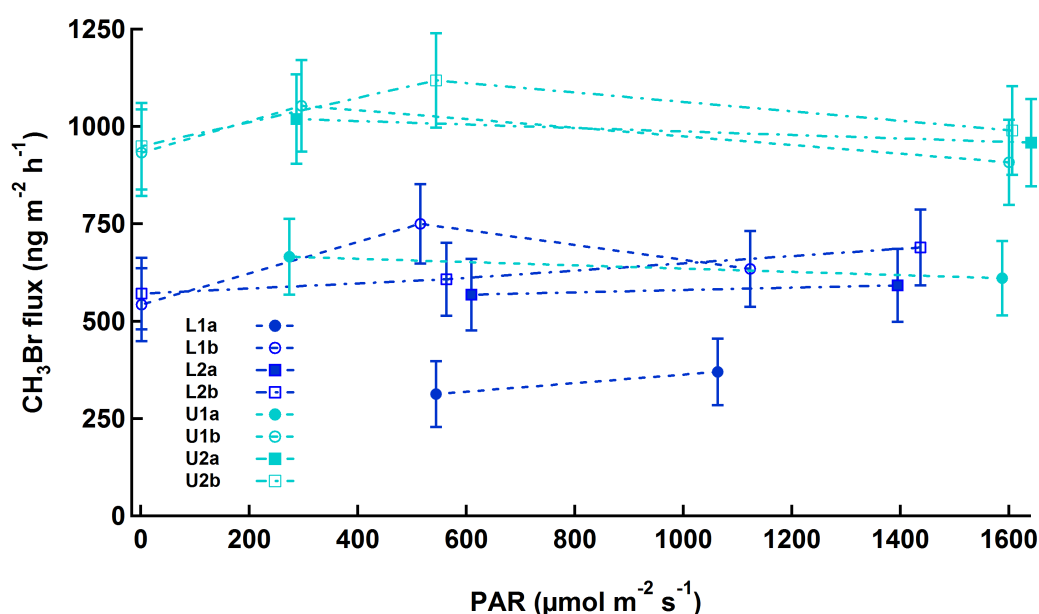
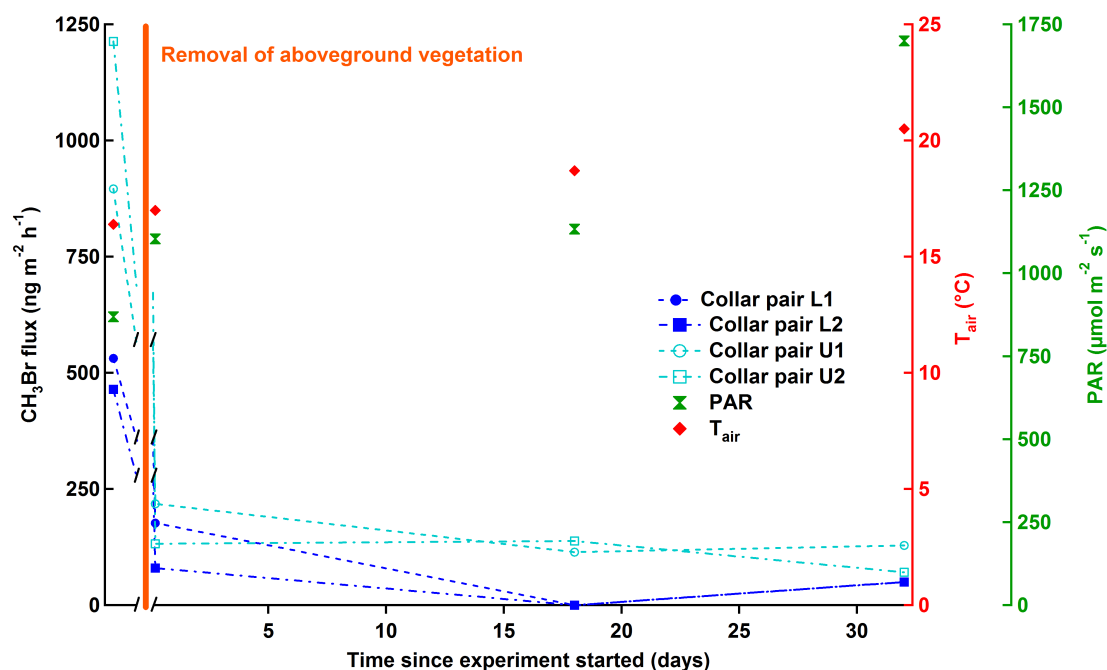


Figure 3.35: Net CH_3Br fluxes versus PAR intensity measured for the collars at Heckie's Hole in the shading experiment on the 31st May 2009. Whiskers incorporate both analytical and sampling uncertainties.

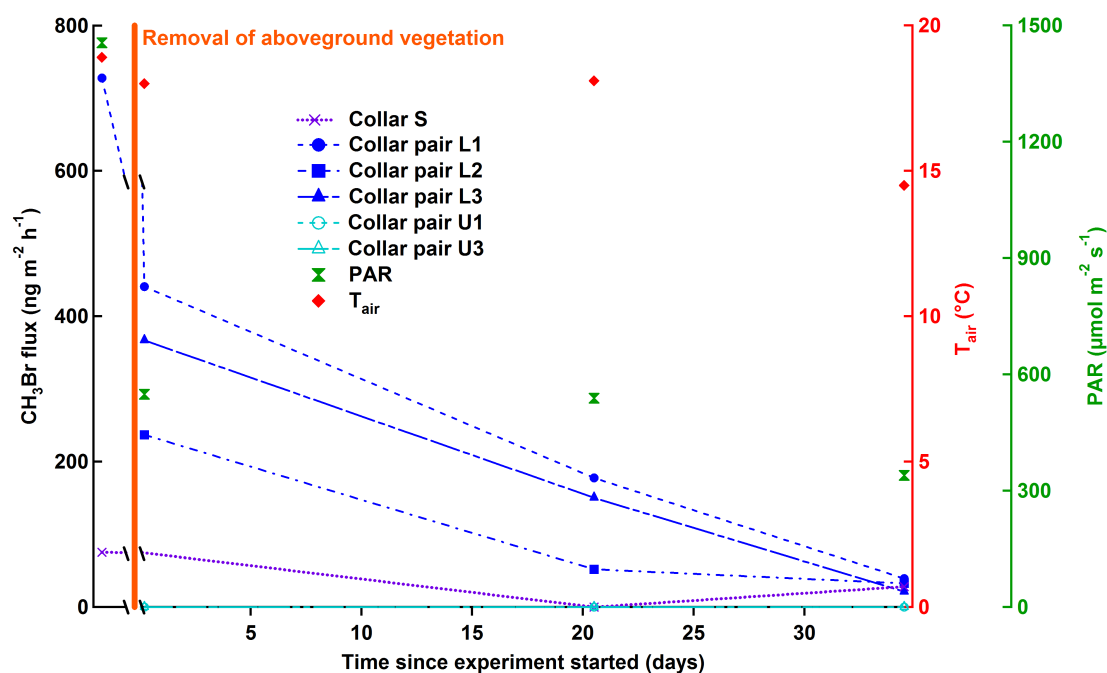
3.4.6 Vegetation removal experiment

CH_3Br measurements obtained during the removal experiment are presented in Figure 3.36. The vertical orange bar denotes when above-ground vegetation was removed. On the first day of the experiment measurements before vegetation removal were not made at all collars at Hollands Farm due to lack of time. At Hollands Farm the fluxes for collar S—which did not contain any vegetation—are also shown.

CH_3Br Measurements conducted a few minutes after complete vegetation removal revealed decreased net CH_3Br emissions for each collar at both sites. However in most collars flux values did not drop to zero immediately but either slowly declined below $50 \text{ ng m}^{-2} \text{ h}^{-1}$ at Hollands Farm or stayed at relatively low levels ($< 170 \text{ ng m}^{-2} \text{ h}^{-1}$) at Heckie's Hole during the following four weeks. CH_3Br emissions at Hollands Farm declined to similar values as measured for collar S which did not contain any vegetation. This could indicate that emissions after above-ground removal were due to the soil rather than the remaining plant material. Paired one-tailed t -tests were applied to each salt marsh dataset to determine whether net fluxes fell significantly after vegetation removal. For comparison, at Heckie's Hole the values measured on the 18th June before and after plant removal were used. For Hollands Farm the last values taken for each collar before vegetation removal and the fluxes measured after removal on the 16th June were used. For both Heckie's Hole and Hollands



(a) Heckie's Hole from 18th June 2009.



(b) Hollands Farm from 16th June 2009.

Figure 3.36: CH_3Br fluxes during vegetation removal experiment started on the 18th June 2009 at Heckie's Hole and 16th June 2009 at Hollands Farm. The methyl halide flux values shown are the average for each collar pair and are presented together with mean ambient air temperatures and PAR measured during sampling days.

Farm net CH₃Br fluxes before vegetation removal were significantly larger than fluxes after removal ($P = 0.001$ and $P = 0.003$ respectively).

A two-tailed t -test comparing the CH₃Br fluxes measured at Hollands Farm at the end of the experiment for all collars originally containing vegetation with all CH₃Br seasonal flux measurements at collar S showed no statistically significant difference between the mean values of the two datasets. This indicates that net-fluxes from collar S are a representative measure of fluxes from the soils in all collars at Hollands Farm, and that plants and not soils are the main emitter of CH₃Br.

CH₃Cl (not shown) Unlike CH₃Br fluxes, flux data of CH₃Cl are not available for the beginning of the removal experiment and so are not presented in a graph. After vegetation removal fluxes in both salt marshes dropped to values near or below the LOD. At Hollands Farm CH₃Cl uptake at some collars was recorded. One-tailed t -tests showed that CH₃Cl fluxes for both salt marshes were significantly lower after plant removal ($P = 0.0001$ for Heckie's Hole and $P = 0.001$ for Hollands Farm).

Summary Net CH₃Br emissions declined within minutes upon plant removal but methyl halide emissions mostly did not fall below LODs. However, only above-ground vegetation was removed and this could explain why methyl halide emissions continued for several weeks after commencement of the experiment, as plant constituents below ground (i.e. roots) could have continued to produce methyl halides. Plants did not die off instantly after above-ground vegetation removal as new shoots had to be removed each time measurements were taken suggesting this the most likely explanation for the continuing methyl halide production. Other factors such as PAR or ambient air temperature cannot explain the drop in emissions in both gases. Apart from PAR on the first day of the removal experiment in Hollands Farm both PAR and ambient air temperature either stayed constant or rose slightly over the duration of the experiment.

3.4.7 Greenhouse experiment

Throughout the 17 d of the greenhouse experiment CH₃Br gross fluxes from plant pots (measured against the mean net flux value of the two bare sand pots) ranged from below LOD to 139 ngg⁻¹ h⁻¹. Fluxes from the two pots containing *Plantago maritima* were often near or below LOD and will not be discussed further. The raw flux data from the experiment were treated mathematically to derive two different data sets.

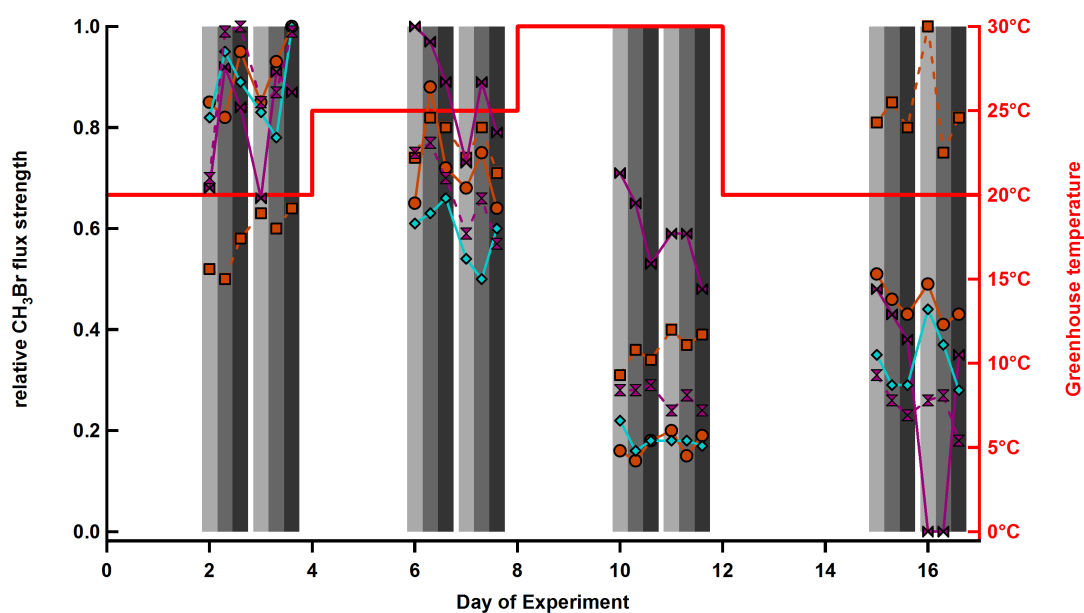
In the first dataset all fluxes for a particular plant pot were normalised to the maximum flux measured for that pot during the entire experiment, shown in Figure 3.37a. This data set was used to assess the influences of diurnal patterns and PAR levels on CH₃Br fluxes. The average uncertainty in normalised flux values was 0.1.

In the second dataset raw fluxes were first adjusted for any time-dependent drift and then normalised (Figure 3.37b). The reason for applying time adjustment was that measurements made during the preparation of the main experiment had revealed dramatic changes in fluxes over time, most likely due to changes in the bromine concentrations in the plants and sediments caused by watering the pots. Furthermore it was not certain if other factors such as plant growth would alter fluxes during the 17 d of the experiment. For this purpose the initial flux measurements at 20 °C were compared with the measurements at the same temperature at the end of the experiment. Assuming that any change in CH₃Br flux for a pot was linear over time an adjustment factor was derived. This adjustment factor was then multiplied by the time elapsed since the start of the experiment and the product subtracted from the raw CH₃Br fluxes to calculate time-adjusted fluxes. In the second step the time-adjusted data set was again normalised to the maximum time-adjusted flux for each plant pot. This dataset was used to assess temperature influences on CH₃Br fluxes. The average uncertainty in adjusted and normalised flux values was 0.1.

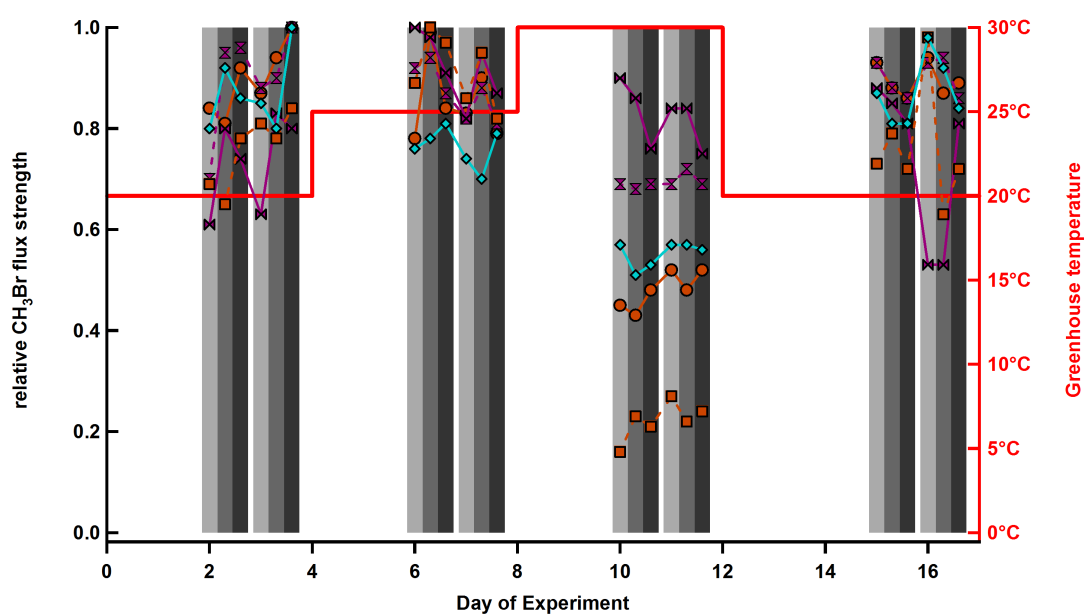
Concentrations measured from the two bare sand pots used as blanks changed during the length of the experiment from 7 to 51 pptV. Concentration differences between the two concurrent blank samples were on average only 5 pptV, but on one occasion 17 pptV. Concentrations were first increasing during the initial 20 °C and the following 25 °C treatment before sharply decreasing during the 30 °C and the beginning of the final 20 °C treatment before increasing again. This indicates that the temperate regime had a marked effect on CH₃Br emissions from the sand itself although it is unlikely that it sustained an appreciable microbial community. Although noticeable in itself no explanation can be given for the observed behaviour.

Raw, untreated flux values from the 5 pots described here were different in magnitude. Fluxes from the mixed *Puccinellia maritima*/*Armeria maritima* pots ranged between 15–130 ng g⁻¹ h⁻¹ similar to the range of fluxes measured for *Triglochin maritima* (21–139 ng g⁻¹ h⁻¹) but considerably larger than fluxes from the single pot of *Agrostis gigantea* with measured fluxes ranging between 0–36 ng g⁻¹ h⁻¹.

PAR and diurnal patterns There were no significant differences in CH₃Br emissions between daytime measurements with and without light nor between daytime and night-time measurements for any individual pot (paired two-tailed *t*-test at *P* = 0.05).



(a) Normalised fluxes.



(b) Normalised time-adjusted fluxes.

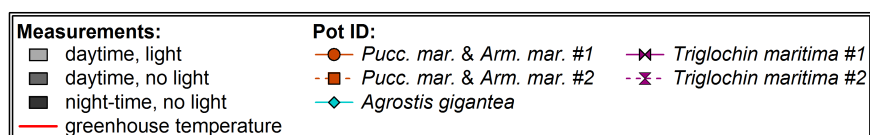


Figure 3.37: Normalised and adjusted CH_3Br fluxes from greenhouse grown plant species. Fluxes were measured against the mean bare sand values as blanks.

Air temperature CH_3Br fluxes had an unexpected relationship with temperature. It was expected that fluxes should increase with rising temperatures. The only notable variation in fluxes was found between 25 and 30 °C. However, instead of rising, fluxes at 30 °C fell on average by 0.3 relative to fluxes at 25 °C. Pots containing a mixture of *Puccinellia maritima* and *Armeria maritima* showed the greatest decline by up to 0.7. The most likely explanation of this behaviour is reduced plant activity caused by stress due to the elevated temperatures. Therefore in order to more fully investigate the effect of temperature on CH_3Br fluxes it would have been beneficial to start the experiment at 10 °C and increase temperatures to either 20 or 25 °C rather than 30 °C.

Summary Overall the results from the greenhouse experiment suggest that neither PAR nor temperature are direct drivers of CH_3Br fluxes, although a link between time of day and CH_3Br fluxes was found during the summer diurnal studies in the field. It has to be kept in mind that temperatures in the greenhouse experiment were changed over a rather narrow range of 10 °C, which might not have been enough to observe a notable effect.

3.4.8 Scale-up of net methyl halide fluxes

Taking into account the results reported in this chapter a tentative estimate of global net methyl halide emissions from salt marshes is made. However, before explaining the steps taken to derive a single global measure for both CH_3Br and CH_3Cl for salt marshes some of the assumptions and issues involving this scale-up are discussed.

Firstly, there is a genuine lack of reliable spatial data on the global distribution and area of salt marshes. This is because salt marshes occur mainly as thin stretches along coastlines and do not reach very far inland. They therefore rarely constitute the dominant vegetation type in the squares of large scale grids used in global remote sensing approaches or GIS datasets. As far as can be ascertained there has also not been any concerted attempt to collate regional scale data on salt marsh area to obtain a global estimate. Therefore the global salt marsh area figures used here are derived from two studies, both of which give a rough estimate only. The first study by Woodwell et al. [1973] estimated the area of global salt marshes and mangroves as $0.38 \times 10^{12} \text{ m}^2$ by extrapolating data from US coastlines to a global scale. However in this study the authors noted specifically that they would be surprised if this estimate was accurate within 50 %. In the second, more recent, study by Costanza et al. [1997] it is not discernible how the estimate of $1.65 \times 10^{12} \text{ m}^2$ for global salt marshes and mangroves was derived. Moreover, the global area of salt marsh estimated in the two studies differs by more than a factor of 4.

Secondly, it was assumed that methyl halide fluxes for salt marshes and mangroves globally exhibit similar patterns to the two sites studied here and that any influence of temperature or light variations with changing latitude is negligible. This assumption is particularly important since both factors will almost certainly have at least an indirect effect on methyl halide emissions through different durations of growing seasons, plant species and plant biomass.

Scaling up was conducted in 7 steps.

1. Seasonal net flux data from the 2 years of measurements for each collar at both sites was pooled into one hypothetical year with 365 Julian days. For each day methyl halide fluxes for every collar were derived—if not already available from measurements—by linear interpolation between recorded flux data, resulting in 365 data points for CH_3Br and CH_3Cl for each collar.
2. For both salt marsh sites on each day, a mean methyl halide flux value, representing the entire salt marsh area, was derived by spatially-weighted averaging of fluxes from individual collars. Spatial weighting was based on the proportion of a vegetation zone relative to the total salt marsh area. The formula was

$$F_{\text{spatial average}} = \sum (F_i \times A_i)$$

where $F_{\text{spatial average}}$ is the weighted mean methyl halide flux for the whole salt marsh and F_i is the methyl halide flux for each individual collar derived from interpolation of the seasonal flux data. A_i is either the relative proportion of a vegetation zone represented by a collar, or if a vegetation zone is represented by n collars, the n -th part of the relative proportion of a vegetation zone to the total salt marsh area ($0 \leq A_i \leq 1$).

3. For both sites the number of hours of daylight and darkness for each Julian day were calculated by using the formula

$$\cos \chi = \cos(\text{LHA}) \times \cos(\text{LAT}) \times \cos(\text{DEC}) + \sin(\text{LAT}) \times \sin(\text{DEC})$$

where χ is the solar zenith angle at a given time of day at a given geographical location, LAT is the latitude of the measurement site, DEC is the declination of the Earth to its orbital plane on that Julian day and LHA is a measure of the time of day. By setting $\cos(\chi)$ to 1 and solving for LHA the length of a day as the time between sunrise and sunset was derived.

4. For each site the average ratio of night-time to daytime methyl halide fluxes ($r_{\text{night/day}}$) was calculated separately for the growing and non-growing season.

5. For each Julian day the flux in $\text{ngm}^{-2} \text{h}^{-1}$ was calculated from the interpolated, spatially averaged fluxes, the length of daytime and night-time hours and the ratio of night-time/daytime fluxes. The average hourly flux was calculated as shown below.

$$\bar{F} = \frac{\sum_{j=1}^{365} ((t_{j, \text{daytime}} \times F_{j, \text{spatial average}}) + (t_{j, \text{night-time}} \times F_{j, \text{spatial average}} \times r_{j, \text{night/day}}))}{24 \times 365}$$

Here \bar{F} is the mean annual methyl halide flux, $t_{i, \text{daytime}}$ and $t_{i, \text{night-time}}$ is the length of time between sunrise and sunset or between sunset and sunrise, respectively, for each Julian day.

6. Standard deviation values for the annual emissions from each site were derived by multiplying average relative standard deviation values from the seasonal fluxes by the annual mean flux values.
7. The mean of the annual methyl halide fluxes from Heckie's Hole and Hollands Farm were multiplied by the estimated global salt marsh area. For the resulting global estimates no standard deviation values are given since it is felt that they would imply an unrealistic level of precision.

The resulting mean annual fluxes for Heckie's Hole were $335 \pm 45 \text{ ngm}^{-2} \text{h}^{-1}$ for CH_3Br and $733 \pm 280 \text{ ngm}^{-2} \text{h}^{-1}$ for CH_3Cl . Drewer et al. [2006] reported an annual mean flux of $350 \text{ ngm}^{-2} \text{h}^{-1}$ for CH_3Br at Heckie's Hole and there is therefore a good agreement between the two studies. Mean annual fluxes for Hollands Farm were somewhat lower at $264 \pm 44 \text{ ngm}^{-2} \text{h}^{-1}$ for CH_3Br and $591 \pm 253 \text{ ngm}^{-2} \text{h}^{-1}$ for CH_3Cl .

Taking the mean of fluxes from both sites resulted in a flux estimate of $300 \pm 44 \text{ ngm}^{-2} \text{h}^{-1}$ for CH_3Br and $662 \pm 266 \text{ ngm}^{-2} \text{h}^{-1}$ for CH_3Cl and a $\text{CH}_3\text{Cl}/\text{CH}_3\text{Br}$ net flux mass ratio of 2.2. Scaling up to the global salt marsh area estimates of Woodwell et al. [1973] and Costanza et al. [1997] values of 1.0 and 4.3 Ggyr^{-1} for CH_3Br and 2.2 and 9.6 Ggyr^{-1} for CH_3Cl were derived.

Using the estimated annual global turnover of $\sim 200 \text{ Ggyr}^{-1}$ for CH_3Br and $\sim 4400 \text{ Ggyr}^{-1}$ for CH_3Cl [Clerbaux et al., 2007] implies that salt marshes account for 0.5–2.2 % of global annual CH_3Br emissions but only 0.05–0.22 % for global CH_3Cl emissions. Taking the possible effects of enclosure time into account fluxes could be up to 1.5 times higher resulting in global salt marsh contributions to CH_3Br and CH_3Cl production of up to 3.2 % and 0.33 % respectively. These global estimates are orders of magnitude lower than the estimates of $14\text{--}24 \text{ Ggyr}^{-1}$ for CH_3Br and $160\text{--}170 \text{ Ggyr}^{-1}$ for CH_3Cl based on measurements from Californian salt marshes

[Rhew et al., 2000; Manley et al., 2006]. However these two studies were conducted in a Mediterranean climate and used less refined up-scaling methods which would have resulted in erroneously high global flux estimates. It is therefore likely that the global flux from salt marshes will lie somewhere between the value derived in this study and the other, higher estimates. Overall it is likely that salt marshes are a globally important source of CH_3Br and only a minor source of CH_3Cl .

3.5 Conclusion

Net fluxes of both CH_3Br and CH_3Cl were strongly seasonal with highest values in summers and lowest values in winters. This pattern is likely linked to general plant growth and therefore indirectly related to temperature and light levels. A similar but weaker diurnal pattern was also observed.

From the literature review it was expected that by careful design of experimental procedures and collection of a large enough data set either a single or a set of environmental factors, such as sunlight, temperature, vegetation composition, soil water content or halide ion content, could be identified as drivers for both the magnitude and pattern of methyl halide emissions in salt marshes. Indeed at both salt marshes there was a significant relationship between the dry weight of plant species such as *Puccinellia maritima*, *Aster tripolium*, *Juncus gerardi* or *Plantago maritima* or the relative elevation and the magnitude of average methyl halide fluxes. Halogen content in plant tissue was not a good predictor of methyl halide emissions from a particular stand. Nor was there any other general relationship between measured environmental drivers and methyl halide fluxes. For instance net CH_3Br fluxes during the growing varied significantly when collars were subjected to different light levels, but CH_3Cl fluxes did not show the same statistical behaviour.

Plants were identified as the main producer of methyl halides in salt marshes with soils being a minor source, corresponding with previous findings. During the non-growing season or after removal of above-ground vegetation, emissions dropped to or near zero. The same was true at night when fluxes again would fall considerably. Therefore a sinusoidal pattern of seasonal and diurnal fluxes was observed.

Experiments under controlled conditions did not clarify the drivers of net methyl halide fluxes from salt marshes. Indeed it seems that greenhouse experiments on salt marsh plants are not a good way to predict plant behaviour in field settings because they do not replicate the complex interplay of factors such as different salt water inundations, soil physical and chemical properties and associated micro-biological communities in the field.

Production of CH_3Br and CH_3Cl appeared to be generally driven by the same molecular mechanism with a significant correlation between the two net gas fluxes occurring in three-quarters of all collars.

Salt marshes are—despite ubiquitous amounts of halide ions—globally only a minor source of CH_3Br and a negligible one for CH_3Cl , although this is principally due to the very small proportion of land globally that comprises salt marsh. Although the generally high amounts of bromine and chlorine in salt marsh vegetation do result in high methyl halide emissions for a given mass of plant material, in general there was no relationship between halide content in plants and methyl halide emissions measured in field studies. Instead methyl halide production by plants seemed more dependent on general environmental conditions, in particular their position within a marsh relative to the high water mark.

The two salt marsh measurement sites represented different physical environmental settings. Soils at Heckie's Hole were more developed than at Hollands Farm, containing more SOM and being generally wetter. Vegetation at Heckie's Hole was reasonably homogeneous whereas at Hollands Farm it was clearly divided into different zones according to proximity to the mainland or distance from the coast. Given these strong differences fluxes from the two sites varied less than would be expected and mean annual weighted fluxes for the two sites were very similar. There was also good agreement between the CH_3Br fluxes measured in this study and those reported by Drewer et al. [2008] at Heckie's Hole which increases confidence in applying an overall average for methyl halide fluxes to all temperate salt marshes and justifies a scaling up based on such an approach.

Overall it appears that global emissions from salt marshes can be satisfactorily described but not modelled. The production of future global emission scenarios of methyl halides from salt marshes in the light of anthropogenic climate change beyond the possible loss of salt marsh habitats due to rising sea levels is likely to prove elusive since the system is too complex.

Chapter 4

Fluxes from plant litter in temperate forests

4.1 Introduction

4.1.1 Previous work

Temperate forests account for a global land cover area of $27.9 \times 10^{12} \text{ m}^2$ [Matthews, 1997; UNESCO, 1973] and have the potential to produce or destroy large amounts of methyl halides through a number of sources and sinks. Potential sources include higher plants [Drewer et al., 2008], forest soils [Dimmer et al., 2001; Drewer et al., 2008], litter [Drewer et al., 2008; Hamilton et al., 2003; Wishkerman et al., 2008], and the fungi often associated with litter [Watling and Harper, 1998; Lee-Taylor and Holland, 2000] whereas reported sinks comprise of forest soils [Rhew et al., 2003; Serca et al., 1998] and higher plants [Jeffers et al., 1998].

Of these four forest components this chapter concentrates on small non-woody detritus (leaves and needles) and its potential fluxes. The reason for this interest is that even small fluxes per unit area would potentially result in sizeable global fluxes when considering the global extent of temperate forest cover. Moreover, there are to date no field data on CH_3Cl fluxes from temperate forest litter although it has been shown to be a potentially important source of CH_3Br by Drewer et al. [2008]. These workers' data, based on 35 samples of deciduous and 19 samples of coniferous litter, showed a mean CH_3Br flux of $43 \pm 33 \times 10^{-3} \text{ ng g}^{-1} \text{ h}^{-1}$ and $80 \pm 37 \times 10^{-3} \text{ ng g}^{-1} \text{ h}^{-1}$, respectively.

Hamilton et al. [2003] and Wishkerman et al. [2008] reported on laboratory studies describing an abiotic emission process for methyl halides suggesting that CH_3Cl and CH_3Br fluxes negatively correlate with leaf litter water content and this was also tested.

4.1.2 Field Locations

Measurements for this study were conducted at three different sites located in Scotland.

Fir Links The main site of this study was a 2.05 ha mixed beech (*Fagus sylvatica*) and sycamore (*Acer pseudoplatanus*) forest (N56°0.1' W002°35.7') planted in 1954. The site is part of the larger Fir Links forest consisting of both deciduous and coniferous trees, in John Muir Country Park, adjacent to Heckie's Hole salt marsh discussed in Chapter 3. The site is not cleared of smaller debris and has a perennial layer of leaf litter covering most parts of the forest floor (Figure 4.1). During the study, ground vegetation was sparse and consisted in some areas of ferns of varying density. Topographically the site had very few features, since it was sited on a plateau a few metres above sea level. The only localised difference discernible was a varying depth of litter layer due to shallow ground depressions and rises and transport by wind. Samples were taken on 16 occasions throughout the years 2008 and 2009.



Figure 4.1: Fir links forest during summer and winter.

Griffin Forest The second site used for this study was Griffin Forest (N56°37' W003°38'), a Sitka spruce (*Picea sitchensis*) plantation of 3 862 ha planted in 1981 in Perthshire near the town of Aberfeldy on a hillside 350 m above sea level [Ibrom et al., 2006]. The location used was partially within a thinned and an un-thinned section of the plantation extensively used by the University of Edinburgh for teaching and research purposes. On two occasions a set of ten samples was collected; however sampling problems led to the loss of the first set of measurements. The second sample set was split into 5 samples each from the thinned and the un-thinned sections of the forest.

Hermitage of Braid One sample of fresh oak leaves (*Quercus robur*) was taken from the Hermitage of Braid (N55°55' W003°12'), a nature reserve of 56 ha situated within Edinburgh [Drewer et al., 2008] on the 21st May 2008.

4.2 Methodology

4.2.1 Leaf litter enclosures

The enclosures used were opaque 12 L polypropylene buckets with air-tight lids and a sampling port made of a 1 mL syringe fitted with an approximately 7 cm long rubber tube that was connected to a three-way valve. Typically 250 to 400 g of fresh leaf litter was placed into each bucket and then enclosed for either 10 min, 1 h, 6 h or 24 h. Depending on the density of the litter layer on the ground, each sample represented a few square metres of forest floor. The number of buckets employed for a measurement ranged from 1 to 18 at any time. Except for measurements at Fir Links on the 30th April 2008 fluxes were measured against a blank sample. A small temperature data logger was employed to monitor the temperature inside a blank bucket during the enclosure period.

4.2.2 Leaf and needle litter density

In order to account for the volume of the litter material enclosed in the chamber the density of both leaf and needle litter was measured. For this purpose approximately 50 g of oven dried leaf/needle litter was placed into a pre-weighed 1 L plastic beaker, the exact mass recorded and then filled with deionised water to soak the litter material for several days. Then the beaker was filled up with more water to the 1 L mark, ensuring that the litter material remained underneath the water line, and the mass was recorded again. The procedure was replicated 6 times for both leaf and needle material and the density calculated from the beaker volume and water and litter mass.

4.2.3 Testing for seasonal and spatial variability of methyl halide fluxes in Fir Links

Normally 3 buckets were filled with leaf litter from a randomly chosen position within Fir Links forest. This was necessary since leaf litter could not be collected from the same spot every time, but meant it was impossible to differentiate between temporal and spatial variations in fluxes. In order to address this problem, on two occasions fluxes were measured

from nine points of a 50 m × 50 m square with sampling points every 25 m in each direction. The data obtained from these two studies were used to compare spatial with temporal variation of fluxes throughout the year.

4.2.4 Dependency of fluxes on enclosure time

As already discussed in Chapter 2, the fluxes measured through the static enclosure method can be dependant on the enclosure time. The accumulation/depletion of CH₃Br and CH₃Cl inside the enclosure can strongly alter the behaviour of the relevant processes and therefore is of importance to the interpretation of any result obtained through this method. Although this is true for static enclosures in general it is even more so for leaf litter enclosures. Emissions from leaf litter were highly variable in magnitude and often very low. This necessitated long enclosure times to achieve concentrations that were more accurately measurable by the analytical equipment. However when emissions were higher than usual longer enclosure times could have altered these fluxes to appear much smaller than they naturally would have been. The enclosure time therefore had to be a compromise between analytical capabilities and preservation of the undisturbed emission process. In order to avoid these pitfalls, measurements of a batch of leaf litter were regularly repeated with different enclosure times. In Fir Links enclosure periods were most often 6 and 24 h whilst all samples in Griffin Forest were enclosed for 10 min and 1 h. The sample from Hermitage of Braid was enclosed for 24 h.

For final comparative interpretation, all fluxes except the single value from Hermitage of Braid were normalized to a specific enclosure time. This was 6 h and 10 min for Fir Links and Griffin Forest respectively. Fluxes at these specific enclosure times were used without modification where they were directly available. Where they were either below the LOD or not available for a specific sample they were derived by normalisation from the longer enclosure measurement.

Normalisation was conducted in 3 steps:

1. All flux pairs (6 h and 24 h for Fir Links and 10 min and 1 h for Griffin Forest) for which both flux values were available and above the LOD were pooled together into a new data-subset.
2. The correlation between flux values from shorter and longer enclosure times in this subset were tested for statistical significance (two-tailed *t*-test, $P = 0.05$) and the mean flux ratio (F_{6h}/F_{24h} for Fir Links and F_{10min}/F_{1h} for Griffin Forest) was calculated.

- Flux values from the longer enclosure times in the full dataset were multiplied by the derived normalisation ratio to gain equivalent flux values at the shorter enclosure times.

More details on the ratios and correlation coefficients are given in Table 4.1 below. It has to

Table 4.1: Ratios and correlation coefficients R used for normalisation of fluxes in Fir Links and Griffin Forest. All correlations shown are statistically significant at $P = 0.05$.

Site	ratio (CH_3Br)	R (CH_3Br)	ratio (CH_3Cl)	R (CH_3Cl)
Fir Links, 6 h/24 h	2.40	0.94	5.71	0.99
Griffin Forest, 10 min/1 h	6.77	0.97	2.16	0.95

be stressed that negative fluxes are necessarily semi-quantitative only since methyl halide uptake was limited by the initial concentrations inside the enclosure and any positive flux from the chamber itself during the enclosure time.

All quoted standard deviation (sd) values combine analytical and concentration-to-flux conversion uncertainties, plus, for mean values, the variation between individual measurements.

4.3 Results and Discussion

4.3.1 Litter characterisation

Total bromine and chlorine analysis via XRF was carried out on mixed bulk samples collected in Fir Links and in Griffin Forest in July 2009 (see Chapter 2 for details). Chlorine content for both samples was below the LOD ($80\mu\text{gg}^{-1}$) whilst bromine content was 11.5 and $3.5\mu\text{gg}^{-1}$ dry wt in Fir Links and Griffin Forest respectively. Bromine content in leaf litter was therefore almost three times the content in the needle litter, probably due to the proximity of Fir Links to the sea. The bromine value for Fir Links was also in good agreement with the value of $8.75\mu\text{gg}^{-1}$ given by Lee-Taylor and Holland [2000] for fine woody matter from coastal regions. However, no other information could be found for bromine content of coniferous trees for comparison to the Griffin Forest data. The fact that chlorine concentrations were below the LOD was surprising since Lobert et al. [1999] had reported mean chlorine concentrations from leaf litter at $\sim 400\mu\text{gg}^{-1}$ dry wt and the Cl/Br mass ratio in natural material would be expected to be ~ 270 [Wiberg, 1995].

Sycamore leaves collected from the forest floor were often infected by *Rhytisma* fungus as described by Drewer et al. [2008] whereas beech leaves seem not to be infected by this fungus. Leaf litter in the lower litter layers were often strongly decomposed and showed extended mycelium biomass.

In Fir Links variation of water content within a sample lot for a given day was often low. Except for the large spatial study in July 2008 leaf litter water content varied by no more than 12 % w/w. In the two more comprehensive studies covering 250 m² on the 9th February 2009 and 28th July 2009 water content varied between 72–80 % w/w and 46–67 % w/w respectively. In comparison mean water content between different measurement days varied between 23 and 77 % w/w and therefore by more than 50 % w/w. One-tailed *F*-tests at *P* = 0.05 comparing the variations from the two spatial studies with the average seasonal results show that variation during the year was significantly greater than the observed spatial variations.

Water content in samples from Griffin Forest strongly depended on the locality where the litter samples were taken. The five litter samples taken from the un-thinned section had a mean water content of 57±2 % w/w whereas the mean water content of the five samples from the thinned section was 36±3 % w/w. A *t*-test at *P* = 0.05 showed that the difference in water content for the two sections was statistically significant.

4.3.2 Methyl halide fluxes

A total of 163 original measurements were made during the years 2008 and 2009 resulting in 87 data for normalised CH₃Br and CH₃Cl fluxes respectively. Individual CH₃Br and CH₃Cl fluxes from all three sampling sites showed a significant correlation at *P* = 0.05 of *R* = 0.80 (*R* = 0.74 significant at *P* = 0.05 when excluding the two extremely high value pairs) with a CH₃Cl/CH₃Br mass ratio of 204 (Figure 4.2). Comparing this value with the CH₃Cl/CH₃Br mass ratio of 22 derived from global CH₃Cl and CH₃Br turnover rates of 4 400 Ggyr⁻¹ and 200 Ggyr⁻¹ respectively [Clerbaux et al., 2007], indicates that litter from temperate forests is likely to be less important for global CH₃Br budgets than for CH₃Cl.

4.3.2.1 Methyl halide fluxes from Fir Links

Mean(±sd) CH₃Br and CH₃Cl fluxes in Fir Links for the entire measurement period were 4.1±3.7×10⁻³ ng g⁻¹ h⁻¹ and 0.98±0.62 ng g⁻¹ h⁻¹ respectively. CH₃Br fluxes ranged between -7.0×10⁻³ to 270×10⁻³ ng g⁻¹ h⁻¹; CH₃Cl fluxes ranged between -0.06 to 33 ng g⁻¹ h⁻¹. No apparent link between fluxes and environmental factors could be discerned. Mean CH₃Br

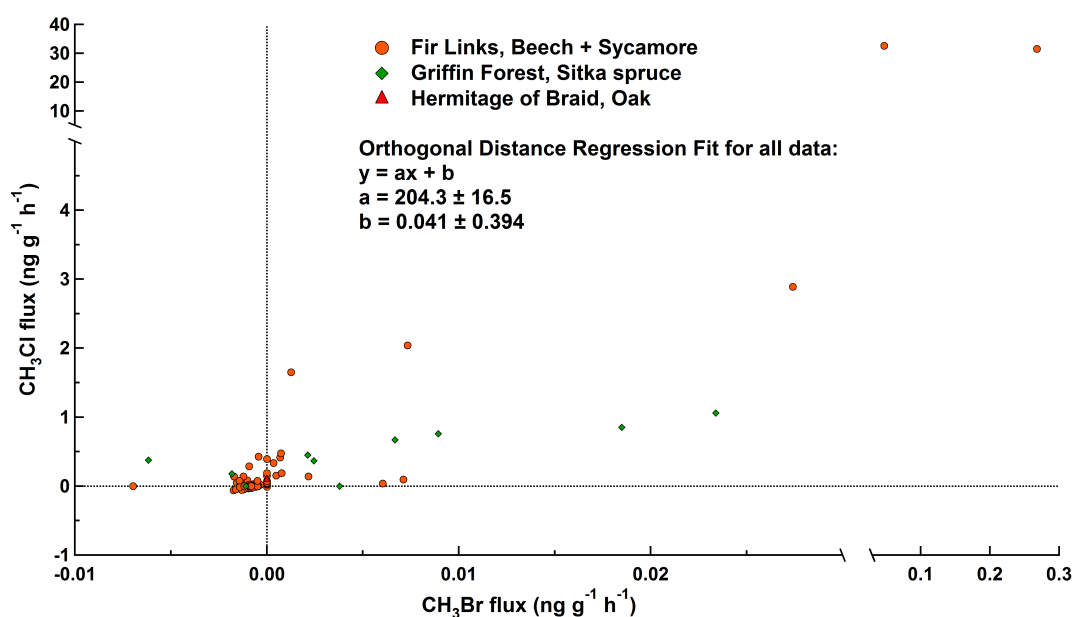


Figure 4.2: Scatter plot of CH_3Cl and CH_3Br litter fluxes measured in Fir Links, Griffin Forest and Hermitage of Braid. All data for Fir Links and Griffin Forest is normalised to 6 h and 10 min enclosures respectively. The data point from Hermitage of Braid was derived from a 24 h enclosure.

fluxes were a magnitude lower than the fluxes reported by Drewer et al. [2008] previously. Moreover, when the highest 3 measured fluxes were ignored, mean CH_3Br fluxes in Fir Links were actually negative ($-3.9 \pm 3.3 \times 10^{-4} \text{ ng g}^{-1} \text{ h}^{-1}$). A possible explanation for the discrepancy between the two studies could be the differences in enclosure duration and the handling of blanks. Enclosure times employed by Drewer et al. were 5–10 min which would most likely result in higher net flux estimates due to better linearity, but potentially at the cost of precision. Secondly, it is not entirely clear if blank fluxes were subtracted from sample fluxes on each occasion. This is important since blank buckets in this study were often found to be small sources of methyl halides and fluxes overall are often very small. The net emissions measured by Drewer et al. could therefore well be unaccounted-for blank fluxes. However, these are speculative reasons and a genuine difference in net fluxes between the two measurement campaigns might exist.

It is not clear whether there is a seasonal trend in fluxes from leaf litter (Figure 4.3). No statistically significant correlation between moisture content, or temperature, and methyl halide fluxes was found. However during the approximately one year of data obtained for Fir Links a sharp spike during August/September 2008 was observed for both CH_3Br and CH_3Cl (Figure 4.3). CH_3Br and CH_3Cl fluxes during this period were up to 100 times and 10 times higher, respectively, than usual. This feature was observed on two consecutive occasions from different parts of the sampling site, making it less likely to be a random occurrence. A possible explanation might be that leaf litter during autumn would start to be replenished by

the trees shedding their leaves for winter. The fresh leaf litter could potentially be a more prolific source of methyl halides than the already strongly degraded material.

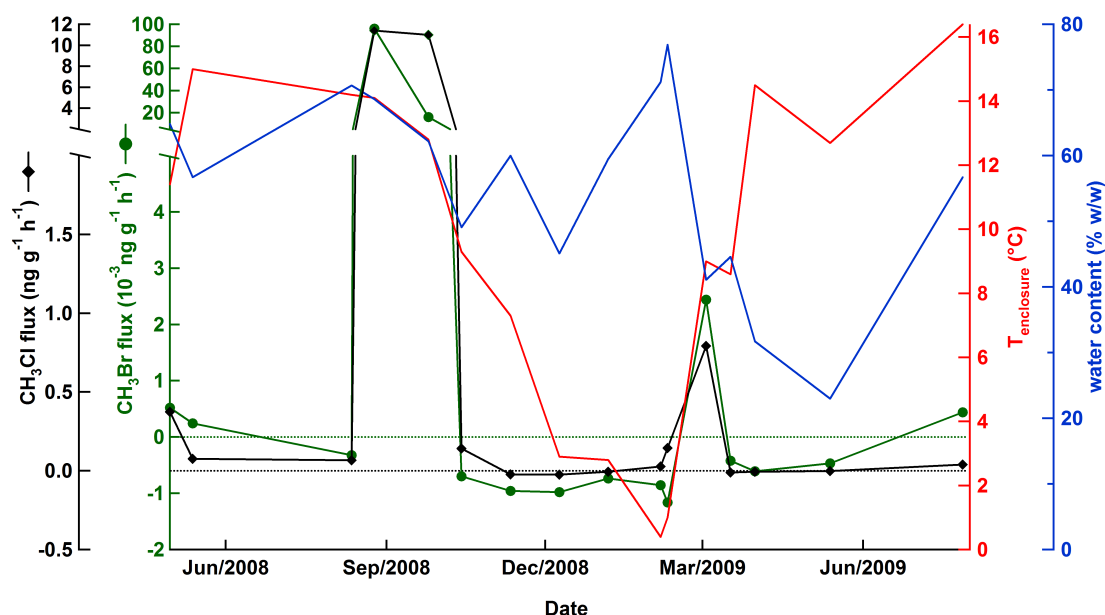


Figure 4.3: Time series of CH_3Br and CH_3Cl litter fluxes at Fir Links during 2008 and 2009. Fluxes are normalized to a 6 h enclosure time. Internal average chamber temperature and leaf litter water content are also shown. Note the break in both the flux axes scales.

Spatial variability The larger studies conducted in Fir Links in February and July 2009 shown in Figure 4.4 indicate that fluxes were not spatially uniform but could vary spatially for a given day between uptake and production, with absolute flux magnitudes varying by 1 to 2 orders of magnitude. As can be seen in Figures 4.4a and 4.4b fluxes of CH_3Br and CH_3Cl in February 2009 showed a roughly similar pattern whereas fluxes of the two gases in July of the same year showed no such spatial correlation (see Figures 4.4c and 4.4d).

Testing for seasonality In order to test whether the spatial flux variation could explain the observed seasonal trends one-tailed F -tests were conducted for both occasions for CH_3Br and CH_3Cl . At a confidence level of $P = 0.05$ it was found that the variability in measurements with time was significantly greater than the variation in fluxes spatially. This therefore indicates that there might be some seasonality in methyl halide fluxes from temperate forest litter.

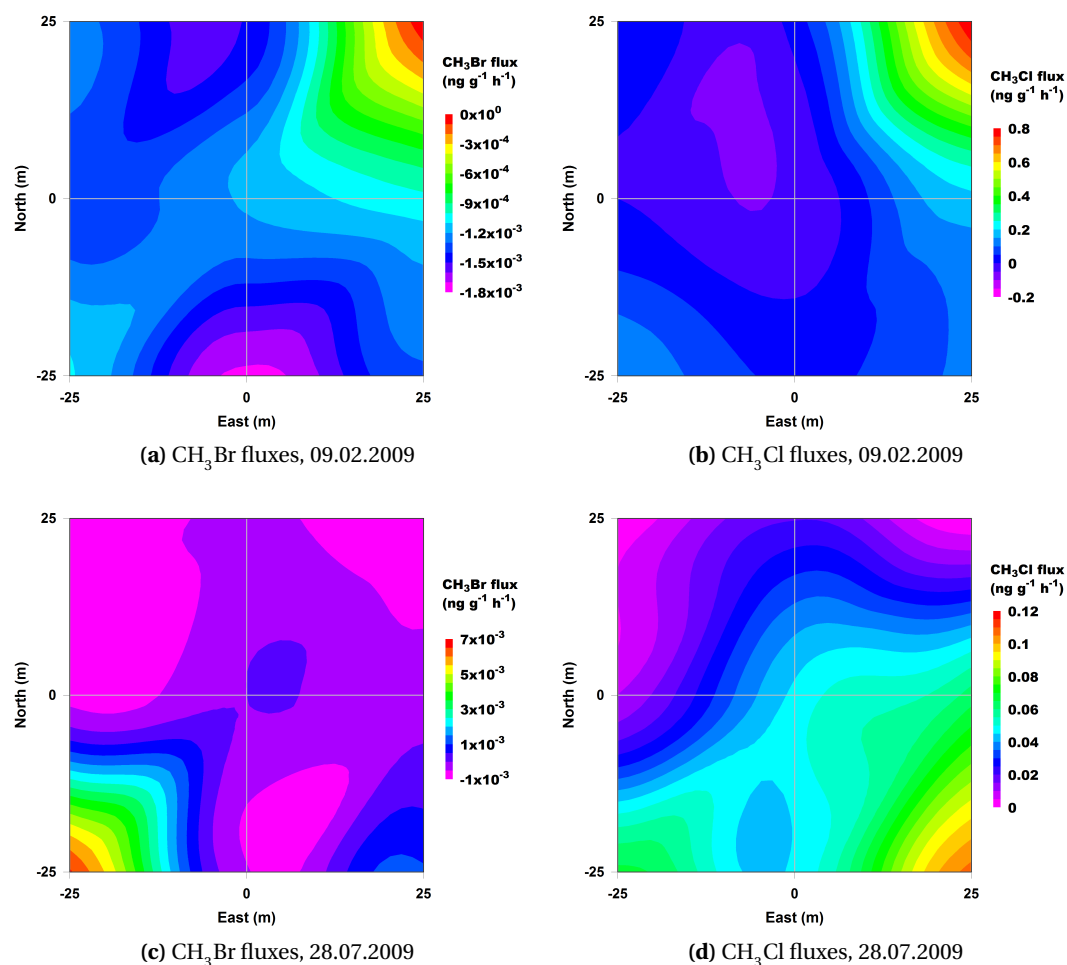


Figure 4.4: Spatial distribution of CH₃Br and CH₃Cl fluxes in Fir Links on the 9th of February 2009 and the 28th of July 2009. Each map was derived by bivariate interpolation from 9 sampling points, each of which was the mean value of two litter samples. Please note that measurements during the two occasions were not conducted on the same spot and therefore cannot be directly compared against each other.

4.3.2.2 Methyl halide fluxes from Griffin Forest

Although methyl halide fluxes from Griffin Forest were measured on two occasions, unfortunately data from only one experiment are usable. The first experiment conducted in February 2009 was based on experiences from Fir Links, so therefore fluxes were anticipated to be low. However methyl halide emissions at Griffin Forest turned out to be so strong that the sampling bags used became contaminated and had to be purged for more than a month before being usable again. On the second sampling occasion, for which data are available fluxes were in general appreciably lower without any explanation for the apparent difference in flux strength.

Mean(\pm sd) CH₃Br and CH₃Cl fluxes in Griffin Forest on the 24th June 2009 were $5.7 \pm 6.3 \times 10^{-3}$ ngg⁻¹ h⁻¹ and 0.47 ± 0.14 ngg⁻¹ h⁻¹ respectively. CH₃Br fluxes ranged from -6.2×10^{-3} to 23×10^{-3} ngg⁻¹ h⁻¹ and CH₃Cl fluxes ranged from 0 to 1.1 ngg⁻¹ h⁻¹, and fluxes of the two gases were significantly correlated at $P = 0.05$ ($R = 0.82$). There was both uptake and production of CH₃Br but only production of CH₃Cl. Again, mean CH₃Br production was only a tenth of what had been observed by Drewer et al. [2008] previously for coniferous litter including samples from Griffin Forest and the above mentioned points are the most likely explanation for this discrepancy. Compared to results from Fir Links in this study mean CH₃Br fluxes in Griffin Forest were of similar magnitude whereas mean CH₃Cl production was only half of that observed for deciduous leaf litter. On the other hand it has to be stressed that only fluxes from the second sampling occasion in Griffin Forest were included and that methyl halide fluxes in Fir Links were dominated by the three highest flux values for both gases whereas absolute fluxes in Griffin Forest were more consistent. No link between flux magnitude and environmental factors was discernible and a t -test indicated no significant difference between fluxes from litter samples in the thinned and un-thinned sections of the forest.

4.3.2.3 Methyl halide flux from Hermitage of Braid

CH₃Br flux for the oak leaf sample collected in the Hermitage of Braid was below the limit of detection and CH₃Cl flux was 0.092 ± 0.034 ngg⁻¹ h⁻¹.

4.3.3 Scale-up of litter fluxes

The data obtained in this study are—although numerous relative to other published studies—still inadequate to give a comprehensive estimate of methyl halide fluxes from global temperate forests. However in order to provide a measure of relative magnitude a simplistic step by step scale up is provided:

Land cover: An estimate of global land cover for temperate forests was derived by taking the area of vegetation classes 10 (cold-deciduous forest, with evergreens), 11 (cold-deciduous forest, without evergreens) and 16 (cold-deciduous woodland) from Matthews [1997] of 15.8×10^{12} m² for deciduous forests and woodlands and the area of vegetation classes 8 (temperate/subpolar evergreen needle-leaved forest) and 14 (evergreen needle-leaved) of 12.1×10^{12} m² for coniferous forests and woodlands.

Estimate of litter pool: Based on model-derived data from Matthews [1997] mean total litter pools (leaf litter plus coarse woody detritus) for vegetation classes 8, 10, 11 and 14 were roughly $3\,700\text{ g m}^{-2}$ whereas total litter pools for vegetation class 16 was $1\,900\text{ g m}^{-2}$.

Leaf litter fraction: The fraction of leaf litter of the total litter pool was assumed to be 30 % as described in Matthews [1997] and Drewer et al. [2008]. The remaining 70 % was made up of coarse woody detritus which was ignored in this study.

Mean methyl halide flux values: The mean flux values from Fir Links and Griffin Forest given above were used to estimate fluxes from temperate deciduous and coniferous forests respectively.

Global fluxes: Multiplication of total areas with leaf litter pools and mean methyl halide fluxes yields an annual production of $1.2\text{ Ggyr}^{-1}\text{ CH}_3\text{Br}$ and $200\text{ Ggyr}^{-1}\text{ CH}_3\text{Cl}$.

Relative contribution to global budgets: Assuming a global annual turnover of $\sim 200\text{ Ggyr}^{-1}$ for CH_3Br and $\sim 4\,400\text{ Ggyr}^{-1}$ for CH_3Cl [Clerbaux et al., 2007], then temperate forests could potentially account for 0.6 % of global CH_3Br production and 4.5 % of global CH_3Cl production.

Taking the data derived from this exercise it can be seen that temperate forests are unlikely to be of relevance for the global CH_3Br budget. However their contribution to the CH_3Cl budget cannot be ignored in closing the current gap. Given that Drewer et al. [2008] found CH_3Br fluxes 10 times of the results in this study, temperate forests might also be a non-negligible source for CH_3Br after all. On the other hand, negative fluxes, especially from the longer enclosure times in Fir Links might be underestimated possibly shifting the balance to lower global flux values.

4.4 Conclusion

This study has reported the first measurements of CH_3Cl fluxes from temperate forest leaf litter. Fluxes in general were found to be of an order of magnitude of $10^{-1}\text{ ng g}^{-1}\text{ h}^{-1}$. Considering the large global area of temperate forests this makes leaf litter a potentially important source of global CH_3Cl . Observed CH_3Br fluxes, augmenting already available measurements, were two orders of magnitude smaller, making leaf litter unlikely to be an important global CH_3Br source. However, previous measurements of CH_3Br suggested that fluxes in temperate forests would be an order of magnitude larger than observed here, with the mostly explanation being differences in sampling method. Furthermore no live plants,

such as trees were included in this study, adding further potential to the importance of temperate forests to global methyl halide budgets.

Methyl halide fluxes from both deciduous and coniferous litter were found to be comparable although bromine content in leaf litter was 3 times the bromine content in needle litter. In general CH_3Cl and CH_3Br fluxes from litter were well correlated at a $\text{CH}_3\text{Cl}/\text{CH}_3\text{Br}$ mass ratio of ~ 200 , 10 times larger than the ratio derived from global turnover estimates. Fluxes in Fir Links from deciduous leaf litter were shown to vary significantly over the duration of a year with respect to observed spatial variability. No apparent driver for emissions was found and it therefore is not possible to predict any future development at this moment.

Chapter 5

Methyl halide fluxes in a tropical rainforest

5.1 Introduction

5.1.1 Literature review

Observations during airborne operations [Gebhardt et al., 2008] and cruises [Yokouchi et al., 2000], together with modelling studies [Lee-Taylor et al., 1998, 2001; Yoshida et al., 2006; Xiao et al., 2009], suggest that there are unaccounted for tropical terrestrial sources of these methyl halides. The *Dipterocarpaceae* (dipterocarps) have recently been identified as one plant family with species that emit significant amounts of CH_3Cl [Saito and Yokouchi, 2008; Saito et al., 2008]. Another possible methyl halide source of global importance is leaf litter [Lee-Taylor and Holland, 2000; Drewer et al., 2008] as discussed in Chapter 4, but this has not been evaluated by *in situ* measurements in the tropics. Laboratory studies have also demonstrated senescent plant material as a temperature-dependent source of methyl halides [Hamilton et al., 2003; Wishkerman et al., 2008].

Prior to this work only two research groups had reported any methyl halide measurements from living tropical plant material. Yokouchi and co-workers [Yokouchi et al., 2002, 2007; Saito et al., 2008] surveyed more than 200 plant species from SE-Asia and found that several plant families including tropical ferns and *Dipterocarpaceae* showed consistently strong CH_3Cl emissions. They also studied the diurnal variation [Saito and Yokouchi, 2006] in both CH_3Cl and CH_3Br fluxes from two ferns and the $\delta^{13}\text{C}$ signature of CH_3Cl [Saito and Yokouchi, 2008] derived from glasshouse grown tropical plants. Saito et al. [2008] compared the emission estimates derived from leaf-scale measurements with concurrent micro-meteorological estimates for a tropical rainforest in Peninsular Malaysia and found that these two were in reasonable agreement. Harper et al. [2003] reported CH_3Cl fluxes and their $\delta^{13}\text{C}$ signatures for two glasshouse grown tropical ferns.

However none of these studies explicitly investigated methyl halide fluxes from tropical leaf litter and the emphasis was almost exclusively on CH_3Cl only. Furthermore, these studies were conducted either in glasshouses or on excised leaves from wild plants enclosed in glass vials for several days. Both of these methods could potentially yield very different results compared with studying intact wild plants. This provided the motivation for this field study, carried out in June and July 2008 in the Danum Valley Conservation Area, near Lahad Datu, Malaysian Borneo, in parallel with the “Oxidant and Particle Photochemical Processes above a South-East Asian tropical rain forest” (OP3) campaign [Hewitt et al., 2010]. Static chamber techniques were used to make the first measurements of fluxes of CH_3Cl and CH_3Br for a number of dipterocarp and other tropical plant species as well as for leaf litter.

5.1.2 Background Information

Dipterocarpaceae are a family of arborescent, pantropical plants [Maury-Lechon and Curet, 1998]. They are a dominating part of many SE Asian rainforests which for this reason are called “dipterocarp forests” but they are also found in lower densities in South and Eastern Asia, Africa and South America. The name of this plant family is derived from Greek (*di*=two, *pteron*=winged, *karpos*=fruit) and consists of between 15–16 genera and 470–580 species. Growing up to and above 80 m in height they constitute “emergent” trees, which means that they grow above the rest of the forest canopy and therefore “emerge” from it. They are commercially important timber trees and have been extensively exploited for this purpose, especially in SE Asia. Unfortunately most of the research conducted on these plants has focused on their silvicultural value so little is known about their physiology that would be useful for this study.

The island of Borneo has the greatest diversity of dipterocarp species in the world and still holds a considerable area of dipterocarp forests. However in recent years these forests have been extensively logged for their timber and to make way for large-scale oil-palm plantations. To study the effect of these dramatic large-scale landscape changes the OP3 campaign was organised by a consortium of mainly British universities and research institutes. The work shown here was conducted in collaboration with this campaign and in particular the University of East Anglia (UEA). The locations used for this study were situated 70 km inland, within the rainforest of Sabah, Borneo, Malaysia, in the Danum Valley Conservation Area (DVCA), at 428 km² one of the largest remaining pristine lowland Dipterocarp forests in SE Asia and at the Innoprise-FACE Foundation Rainforest Rehabilitation Project (INFAPRO), a 300 km² forest rehabilitation project. Both of these areas are, in turn, sited within the *Yayasan Sabah* logging concession area (Figure 5.1). More specifically, the study was conducted in three distinct measurement locations: branch measurements were conducted within the

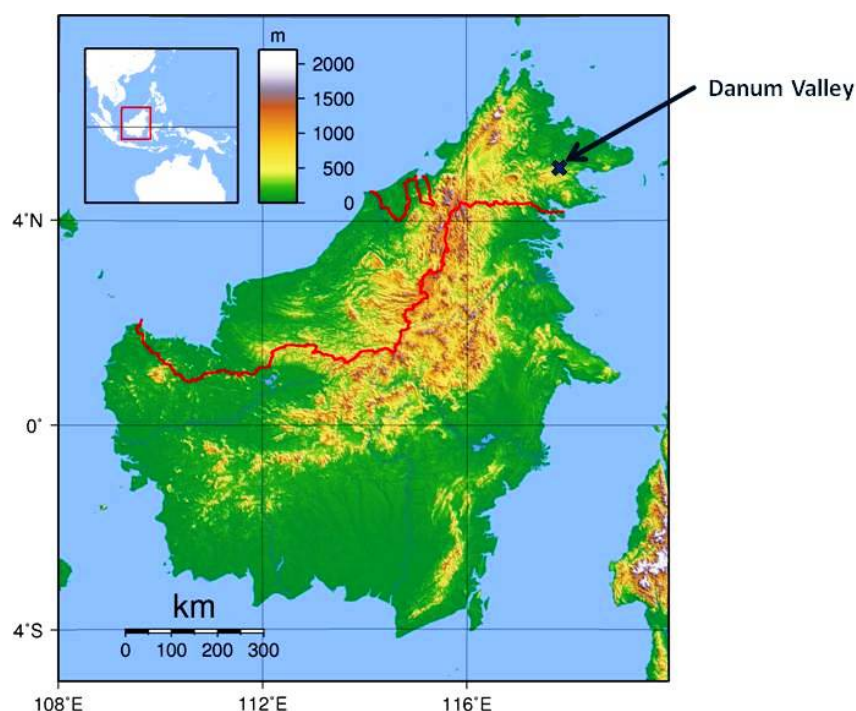


Figure 5.1: Map showing the approximate position of Danum Valley in the State of Sabah, Malaysia, SE Asia. Red lines mark the national borders of Brunei, Malaysia and Indonesia. Retrieved from: http://en.wikipedia.org/wiki/File:Borneo_Topography.png on the 8th January 2010.

grounds of the Danum Valley Research Centre (N4°58' E117°48') [Hewitt et al., 2010], which lies on the eastern fringe of the DVCA, and within the grounds of the INFAPRO nursery (N4°58'49'' E117°50'39''); seedling enclosures were conducted in the INFAPRO nursery; and all leaf litter enclosures were conducted within the West Trail, a signposted area of rainforest adjacent to the Danum Valley Research Centre. In addition, a vertical background ambient air methyl halide concentration profile was taken at the Bukit Atur Global Atmospheric Watch (GAW) tower (N4°58'49'' E117°51'19'') which is an all-steel lattice structure of approximate 100 m height that is part of the World Meteorological Organisation's (WMO) GAW project. All measurements were conducted between the 19th June and the 20th July 2008.

The climate of Borneo is characterised by all-year-round high rainfall without marked seasonality or drought period. Average annual rainfall from 1986 to 2008 inclusive was 2840 ± 438 mm, whilst annual rainfall during 2008 specifically was 3220 mm, as measured at the Danum Valley rain gauge [Hanapi, 2008]. Temperatures recorded during the measurement period ranged from 22.0 °C at night to 30.6 °C during the day time. However, the maximum temperatures were normally measured outside the forest canopy. Temperatures measured inside the canopy ranged from 21.4 °C to 28.4 °C.

5.2 Methodology

Flux measurements were made on branches of free-standing trees and seedlings at the Danum Valley Research Center and at the INFAPRO nursery nearby rather than inside the rainforest itself. The reason for this was that these trees had been planted in open areas. This leads to a different physiology which is necessary for conducting the branch enclosures.

Dipterocarp trees develop from thin seedlings that are growing in large numbers in the shade of their common mother tree. Due to the lack of light available, leaves on such a seedling are very sparse and only grow at its very top. It is therefore perfectly normal to find a 3 m high tree with a 5 cm diameter stem and only a handful of leaves. Only once the mother tree has died and left a reasonably large enough gap of open canopy do these seedlings grow both in height and width and foliage. Any specimen of tree that would be reachable for enclosures (≤ 2.5 m) would not be suitable for measurements because of the lack of foliage mass.

For this reason planted trees were chosen instead. As they have been grown in the open they do not follow the normal physiology of stunted horizontal growth but rather follow the growth pattern seen on most European deciduous trees. The measurement results presented here should therefore be seen as a presentation of the behaviour of an emergent mother tree since both will be subject to similar light levels.

Inside the INFAPRO nursery seedlings were grown for the reforestation of deforested areas as well as for the replacement of selectively logged species inside the logging concession. Each seedling was grown in a small cylindrical volume of soil held together by a plastic foil. These seedlings were then grouped together by species and age in wooden grids that formed rows underneath a tarpaulin that gave shade from the intense sunlight of the open sky. Measurement results from these specimens are most likely to be comparable to smaller trees in the undergrowth of the rainforest since they share similar sunlight levels and physiology.

5.2.1 Branches enclosures

Branches were enclosed in transparent cylindrical chambers of either 26 L volume (Polycarbonate, 52.5 cm length, 25 cm diameter) or 66 L volume (Polyethylene terephthalate, 80 cm length, 32.5 cm diameter), equipped with forced air circulation and supported on tripods. An air-tight seal was achieved by using plastic bags whose base had been cut out and which were sealed around the open end of the chamber and the branch with elastic bands. During the 20 min enclosure time, internal and external air temperature, PAR and total solar radiation were recorded with data loggers. The two light sensors were positioned on a second tripod

<1 m distant from the chamber since light levels were spatially very variable. It is important to note that time of day and solar flux were not directly correlated since the trees were standing in a valley, subject to shading by hillside or other trees according to the angle of the sun. At the end of the enclosure time a 550 mL air sample was extracted and stored in a 1 L Tedlar bag. Contemporaneous samples of ambient air were collected and stored similarly. At the end of the sampling period, the total number of leaves on the enclosed branches were counted and a subset of the foliage removed. The fresh mass of each individual leaf was then determined, the leaves were oven-dried to constant mass at 70 °C and then reweighed. The number of leaves on the individual branches and the average mass of the dried leaves taken from them was then used to calculate the overall dry leaf mass.

A total of 46 enclosure measurements on 17 species was carried out. This comprised both replicate measurements on different individuals of the same species as well as replicates on the same individuals. The majority of species investigated were from the *Dipterocarpacea* family, but *Crateva religiosa* (*Capparaceae*), *Etlingera brevilabrum* and *Etlingera elatior* (*Zingiberaceae*), *Syzygium campanulatum* (*Myrtaceae*) and *Eusideroxylon zwageri* (*Lauraceae*) were also included. The height of sampled branches ranged between 1.5 m and 2.5 m above the ground. Measurements were undertaken during both day and night. No correction was used to account for the plant volume inside the chamber since it was deemed negligible but blank sampling for both chambers was conducted to account for any production or uptake by the chambers themselves. Where there was a significant blank flux this was taken into account for the final flux calculations.

5.2.2 Seedling enclosures

Dipterocarp seedlings of up to 80 cm height were measured in the INFAPRO nursery below a shading screen. For this purpose the 66L branch chamber described above was used in a vertical position with the base of the enclosure comprising of a strong plastic bag that was sealed around the open end of the chamber. For each measurement several seedlings were bound together to make up sufficient leaf mass. In all other aspects the measurement procedure was the same as that for branches. Due to technical difficulties during the sample analysis, results for only two species (*Shorea johorensis* and *Dryobalanops lanceolata*) have been obtained. In order to calculate the final chamber volume the height and diameter of the soil parcels were measured and later subtracted from the empty chamber volume. A correction was also applied for any significant blank chamber fluxes.

5.2.3 Leaf litter enclosures

Leaf litter was collected from seven representative 10 m² plots within the rainforest adjacent to the Danum Valley Field Centre. Each collection area comprised leaf litter from a variety of plant species that were determined on site. Triplicate sub-samples (except for plot A, which was sampled in duplicate) of between 250 and 450 g fresh leaf litter from each location were enclosed (on site) for 24 h in opaque 12 L containers after which a 550 mL air sample was withdrawn and stored in a 1 L Tedlar bag. A parallel blank container held a small data logger that recorded the internal temperature whilst a second data logger recorded the external air temperature at 1.50 m height during the full enclosure period. No correction was applied for the leaf litter volume inside the containers. Leaf litter wet and dry mass was measured as described in Section 2.3.1.

5.2.4 Tower profile measurements

On 10.07.2008 one ambient air sample each was taken at the Bukit Atur GAW tower at ground level (inside the forest surrounding the tower), 15 m and 60 m height. The sampling started at 9:25 am and ended at 10:24 am. The three concentration points were used to construct a concentration profile for both methyl halides. During the period when these samples were analysed blank standards gave zero or very small detector signals on the GC instrument and therefore the concentrations are assumed to be absolute values.

5.2.5 Sample analysis

Gas samples were analysed for CH₃Br and CH₃Cl either directly at Danum Valley on the UEA GC-MS or couriered to the University of Edinburgh for analysis. In the latter case, all samples were analysed within two weeks of collection and the storage temperature during transport was recorded. Sample analysis in Borneo was carried out by Graham Mills; sample analysis in Edinburgh was partially carried out by Catherine Hardacre.

The following is a brief description of the UEA analysis procedure and equipment: Samples were analysed using an automated system comprising of an online air pre-concentrator (UNITY and Online Air Server; Markes International Ltd., Llantrisant, UK) coupled to an Agilent 6890 GC with a MS5973N MS (Agilent Technologies Inc., Santa Clara, CA, USA) operating in either EI or NICI mode and single ion monitoring mode [Worton et al., 2008]. A 500 mL aliquot of each sample was pre-concentrated onto a mixed Carbograph 1 TD/Carboxen 1000 trap cooled to -10 °C with a two-stage Peltier cell. The trap was

then heated to 250 °C to transfer the analytes in high purity helium carrier gas (99.9999 %) onto the RTX-502.2 column, length 105 m, i.d. 0.32 mm (Restek, Bellefonte, PA, USA). The temperature programme was 30 °C for 2 min, heat at 8 °C min⁻¹ to 150 °C, hold for 16 min, heat at 20 °C min⁻¹ to 220 °C, and hold for 5 min. NICI was most commonly used, with a LOD for CH₃Cl of ~30–60 pptV. However, some samples were analysed using EI, with an LOD for CH₃Cl of 0.3 pptV. Accuracy and precision were ±6 % and ±3 %, respectively, for CH₃Cl determination at 45 pptV by NICI or 5 pptV by EI. Calibrations were performed every 8 samples by analysing 500 mL of a gas standard containing atmospheric levels of analytes calibrated against the gravimetric primary gas standards for CH₃Cl and CH₃Br on the 'NOAA 2003' scale (www.esrl.noaa.gov/gmd/hats/standard/scales.html).

5.3 Results and discussion

5.3.1 Branches and seedlings

A summary of the flux measurements from individual tropical species is presented in Table 5.1. The magnitude of the fluxes was highly species dependent. Whilst some plants showed no emissions, the genus *Shorea* showed consistently high fluxes. CH₃Cl emissions from *Shorea agamii*, *Shorea macrophylla*, *Shorea pilosa* and *Shorea superba* were consistently large (flux > 10 ng g⁻¹ h⁻¹) over several measurements, whilst *Shorea johorensis* and *Crateva religiosa* also had large CH₃Cl emissions in single measurements. The *Dipterocarpus applanatus*, *Dryobalanops lanceolata* and *Syzygium campanulatum* species were moderate CH₃Cl emitters (10 ng g⁻¹ h⁻¹ > flux > LOD). CH₃Br emissions were large (flux > 1 ng g⁻¹ h⁻¹) for *Crateva religiosa* and *Shorea pilosa*, whilst *Dipterocarpus applanatus*, *Dryobalanops lanceolata*, *Eusideroxylon zwageri*, *Shorea agamii*, *Shorea falciferoides*, *Shorea macrophylla*, *Shorea superba* and *Syzygium campanulatum* were moderate CH₃Br emitters (1 ng g⁻¹ h⁻¹ > flux > LOD). Mean CH₃Cl and CH₃Br fluxes across the 18 species of plant investigated were 19 (range, <LOD – 76) and 0.4 (<LOD – 2.9) ng g⁻¹ h⁻¹, respectively. Although the linear correlation was not strong, if plants were emitters of one methyl halide they were emitters of the other (Figure 5.2a, $R = 0.42$, $P < 0.004$).

Methyl halide fluxes from five *Dipterocarpacea* species—*Dipterocarpus applanatus*, *Dryobalanops lanceolata*, *Hopea nervosa*, *Shorea agamii* and *Shorea pilosa*—were measured at intervals during the day and once during the night (Figure 5.3). There was evidence of a pattern for largest emissions during mid to late afternoon and continuing, but declining, emissions during the night, particularly for the two strongest emitters, *Shorea agamii* and *Shorea pilosa*. In some instances there was no apparent significant diurnal cycle. For these 5

Table 5.1: Summary of methyl halide net fluxes from living trees in Danum Valley and INEAPRO nursery. The sd values combine analytical and concentration-to-flux conversion uncertainties, plus, for instances where replicate measurements were undertaken, the variation between measurements for a single species. Individual flux determinations have their own LOD value; the interquartile ranges of LOD values for the measurements shown in this table were 1.6–5.3 and 0.053–0.091 $\text{ng g}^{-1} \text{h}^{-1}$ for CH_3Cl and CH_3Br fluxes, respectively.

Species	no. of samples ^a	$\text{CH}_3\text{Cl flux (ng g}^{-1} \text{h}^{-1})$				$\text{CH}_3\text{Br flux (ng g}^{-1} \text{h}^{-1})$			
		mean	sd	min	max	mean	sd	min	max
<i>Cratogeomys religiosa</i>	1	37.1	7.9			2.86	0.53		
<i>Dipterocarpus applanatus</i>	5+1	8.4	4.2	<LOD	11.2	0.1	0.08	-0.1	0.3
<i>Dipterocarpus confertus</i>	1	<LOD	-			<LOD	-		
<i>Dipterocarpus gracilis</i>	1	<LOD	-			-0.025	0.018		
<i>Dryobalanops keithii</i>	1	<LOD	-			<LOD	-		
<i>Dryobalanops lanceolata</i>	4+1+1	4.8	3.1	<LOD	9.5	0.14	0.09	-0.06	0.38
<i>Etilingera brevibrum</i>	2	4.2	5.7	<LOD	8.8	-0.18	0.08	-0.2	-0.17
<i>Etilingera elatior</i>	1	-	-			-0.08	0.05		
<i>Eusideroxylon zuengeri</i>	1	<LOD	-			0.16	0.05		
<i>Hopsea nervosa</i>	4+1+1	1.6	4.3	<LOD	5.6	0.04	0.11	-0.21	0.33
<i>Parashorea malaanonan</i>	1	-2.5	0.6			-0.12	0.05		
<i>Shorea agamii</i>	6+1	71.4	19.3	40.7	114	0.52	0.18	<LOD	1.05
<i>Shorea falciferoides</i>	1	<LOD	-			0.15	0.06		
<i>Shorea johorensis (seedling)</i>	1	36.3	7.9			-0.24	0.15		
<i>Shorea macrophylla</i>	2	76.3	15.1	65.9	86.7	0.51	0.1	0.47	0.54
<i>Shorea pilosa</i>	6	65.3	16.7	29.3	104	2.68	0.65	0.74	4.52
<i>Shorea superba</i>	2	22.4	3.7	22.2	22.6	0.15	0.06	0.15	0.16
<i>Syzygium campanulatum</i>	2	1.7	0.6	1.4	2.0	0.1	0.06	0.05	0.15

^anumber of samples, for example, "5+1" indicates 5 measurements on one individual of the species plus one measurement on a second individual of the species.

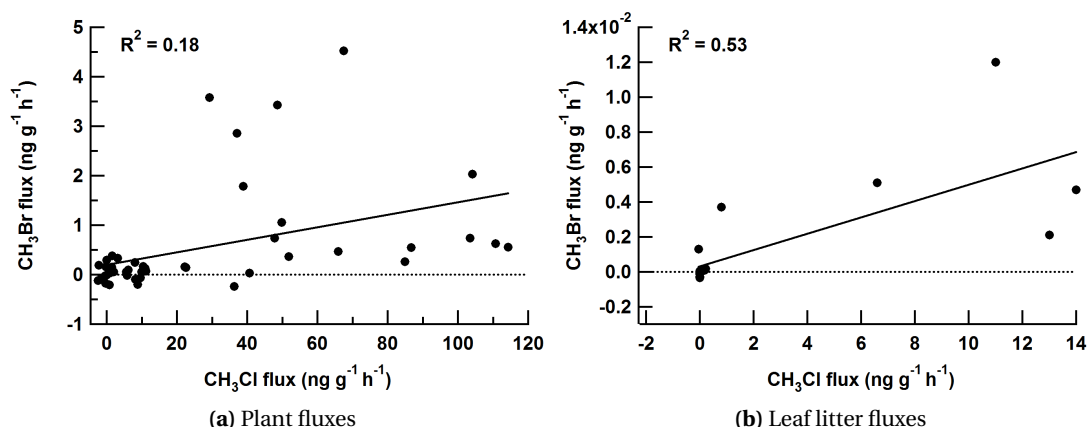


Figure 5.2: Correlations between CH_3Br and CH_3Cl fluxes from (a) individual live plant measurements, (b) individual leaf litter measurements. Note that negative fluxes (net uptake) for litter are only semi-quantitative.

species, there were no significant correlations between methyl halide fluxes and the measured environmental parameters of PAR, total solar radiation, air temperature and internal chamber temperature (although the datasets are comparatively small). Instead, the factor influencing emissions is species.

The data reported here are the first measurements of methyl halide emissions from live species of a number of important South East Asian tropical rainforest species, and the first such CH_3Br fluxes from any dipterocarp species. There is coherence with the findings of Saito et al. [2008], from a different part of South East Asia, that the *Dipterocarpaceae* family is, in general, a strong emitter of CH_3Cl , but that fluxes vary widely between species. Saito et al. [2008] quantified CH_3Cl fluxes from small masses of excised leaves from 117 plant species, including 29 species of the *Dipterocarpaceae* family, following enclosure in 40 mL vials for 4–8 d. Of the 24 species with CH_3Cl emissions greater than $10 \text{ ng g}^{-1} \text{ h}^{-1}$, 19 were dipterocarps with a median CH_3Cl emission rate of $30 \text{ ng g}^{-1} \text{ h}^{-1}$. Here, a total of 41 measurements on 13 species of dipterocarps were carried out with mean emission rates of $30 \text{ ng g}^{-1} \text{ h}^{-1}$ for CH_3Cl and $0.55 \text{ ng g}^{-1} \text{ h}^{-1}$ for CH_3Br . There is therefore good correspondence between the two studies for CH_3Cl . The large emission of CH_3Cl from *Crateva religiosa* measured in this work is also consistent with the observation by Yokouchi et al. [2007] that this species was a strong CH_3Cl emitter, although the flux measured here was somewhat smaller than previously reported.

Analysis of the Cl^- and Br^- content of the plant material enclosed was not possible on site and export of plant material from Borneo is restricted. Watling and Harper [1998] measured Cl^- in wood of 48 tropical species but none were species whose CH_3Cl fluxes were measured in this work, although their measurements did include a few other *Shorea* species whose Cl^-

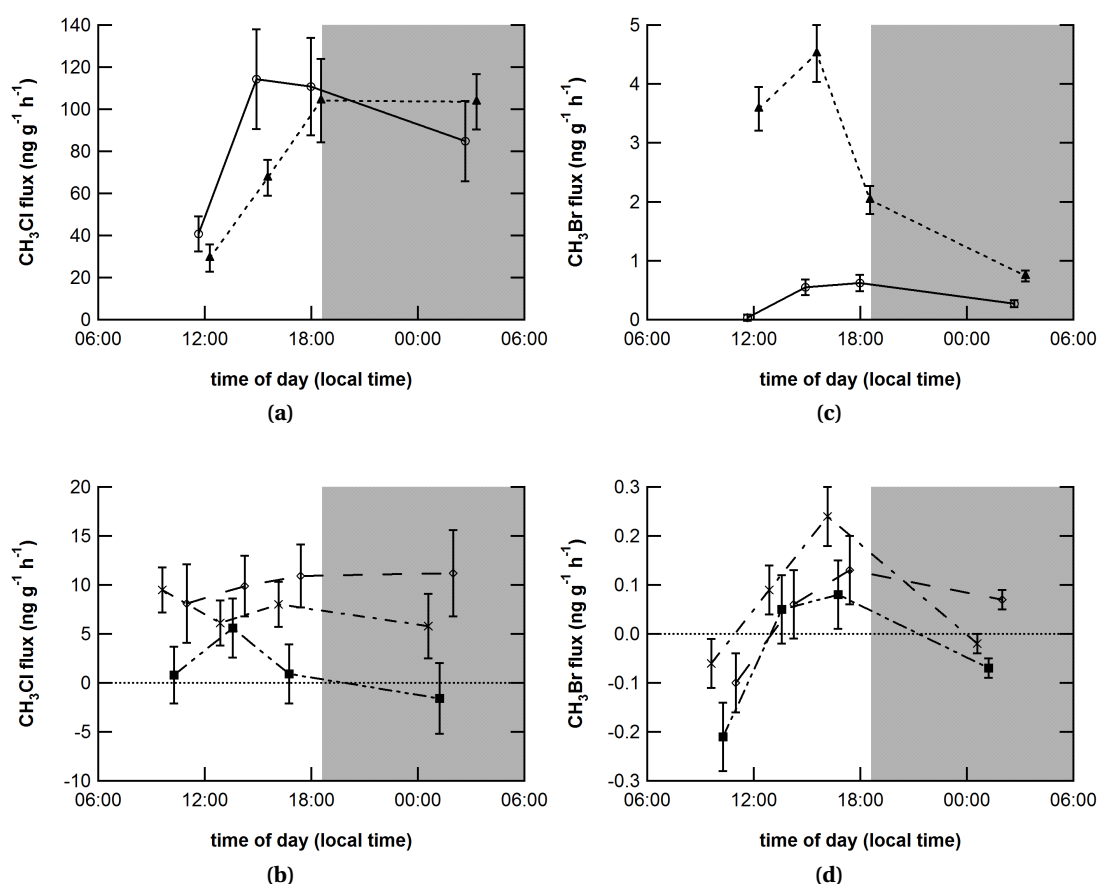


Figure 5.3: Diurnal CH_3Cl and CH_3Br fluxes from five different dipterocarp species at Danum Valley: (a) and (c) *Shorea agamii* (\circ) and *Shorea pilosa* (\blacktriangle); (b) and (d) *Hopea nervosa* (\blacksquare), *Dipterocarpus applanatus* (\diamond) and *Dryobalanops lanceolata* (\times). Whiskers incorporate both analytical and sampling uncertainties. Shaded areas mark hours between sunset and sunrise.

contents were 24, 39, 39, 69 and 187 mg kg^{-1} dwt wood. The range in the Watling and Harper [1998] Cl^- measurements spans more than two orders of magnitude (9 to 1014 mg kg^{-1}) and this range excludes two palm species (as not relevant to this study) with even higher Cl^- content. Overall, the mean Cl^- content for the 46 tropical species was 90 mg kg^{-1} , suggesting that the Cl^- contents of the wood of the measured *Shorea* species were not unusual. Lobert et al. [1999] provide a summary of Cl^- content in tropical (and temperate) wood, foliage and litter separately, again with a large range in individual measurements. Two general trends can be noted from their data: (a) Cl^- content in foliage is higher, on average, than in wood, with litter concentrations intermediate between the two, for both temperate and tropical species; (b) Cl^- content in wood/foliage/litter of tropical species is higher, on average, than in temperate species. Data on Br^- content of plant species are even more sparse. Lee-Taylor and Holland [2000] provide summary Br^- content of 3.7 mg kg^{-1} for tropical coarse wood detritus and 16 mg kg^{-1} for fine wood matter (assumed to include leaf litter) which are values circa one order magnitude lower than the Cl^- concentrations quoted above. As with Cl^- ,

Lee-Taylor and Holland [2000] also report that Br^- content in tropical forest material is, on average, higher than for temperate forest material. Data on variability of halogen content between different parts of the same individual plant or between individuals either in the same location or elsewhere are essentially non-existent.

There is therefore certainly insufficient evidence at present to implicate any link between methyl halide flux and halogen content for dipterocarp species in particular, although the general observation of higher halogen content in plant material from the tropics is consistent with the greater importance to methyl halide emissions generally ascribed to tropical rather than to temperate forests. However, it is known that many vascular plants contain a halogenating methyl transferase enzyme, and that methyl halide emission represents only a small proportion of the halogen content [Manley, 2002], so it seems likely that variation in expression of this enzyme in particular species and individuals will drive variation in methyl halide flux at least as much as intrinsic variation of tissue halogen concentration.

Any attempt at scaling up these plant-scale measurements to tropical rain forests globally is necessarily indicative, order-of-magnitude only. Assuming the leaf biomass per unit area of 900 g m^{-2} presented by Saito et al. [2008] for lowland tropical forest in Peninsular Malaysia is reasonable for similar forests in Malaysian Borneo, then applying the mean CH_3Cl and CH_3Br fluxes of 19 and $0.38 \text{ ng g}^{-1} \text{ h}^{-1}$ across all measured species in this work gives estimates for average canopy basal area CH_3Cl and CH_3Br fluxes of ~ 17 and $\sim 0.34 \mu\text{g m}^{-2} \text{ h}^{-1}$, respectively. Multiplying by an area of $10.4 \times 10^{12} \text{ m}^2$ for tropical evergreen rainforest globally [Guenther et al., 1995] yields global annual emissions of 1.5 Tg CH_3Cl and 30 Gg CH_3Br . These values are probably overestimates since dipterocarp species were deliberately targeted in this work. According to Davies et al. [2003], cited in Saito et al. [2008], dipterocarps comprise $\sim 30\%$ basal area coverage in Malaysian rainforest. Applying the slightly more sophisticated approach of weighting average emissions from dipterocarp and non-dipterocarp species separately, yields estimated basal area CH_3Cl and CH_3Br fluxes of ~ 12 and $\sim 0.2 \mu\text{g m}^{-2} \text{ h}^{-1}$, or estimated global annual emissions of 1.1 Tg and 18 Gg, respectively. These latter values correspond to 25 % and 9 % of the estimated total global annual fluxes of ~ 4.4 Tg and ~ 200 Gg for CH_3Cl and CH_3Br , respectively, summarised by Clerbaux et al. [2007].

5.3.2 Leaf litter

For leaf litter measurements there was generally good agreement in fluxes between the triplicate samples of leaf litter from each sampling location but large differences (up to 4 orders of magnitude for CH_3Cl and 3 orders of magnitude for CH_3Br) between the different locations (Table 5.2). This could be due to different moisture regimes and microbiological

activity of the leaf litter at each plot. Samples at each location were collected on different days and variation in antecedent rainfall caused substantial variation of water in the litter layer on the forest floor. The lack of significant correlation observed here between CH_3Cl and CH_3Br fluxes and water content in bulk field samples of leaf litter ($R^2 = 0.18$ and 0.19 , respectively) contrasts with laboratory work on senescent leaves in which fluxes of CH_3Cl and CH_3Br were negatively correlated with water content [Hamilton et al., 2003; Wishkerman et al., 2008]. A likely explanation for this discrepancy is the different nature of the leaf material used. Hamilton et al. and Wishkerman et al. used intact leaf material that was collected either before the onset or in a very early stage of decay in which the activity of fungi and bacteria was probably negligible. The leaf litter used in this work included substantial decomposing material and leaf-rotting micro-organisms are known producers of CH_3Cl and CH_3Br [Harper, 1985; Moore et al., 2005]. Thus production could be the result of abiotic or micro-biotic activity or both. Despite the wide variation in the flux magnitudes, the significant correlation between CH_3Cl and CH_3Br fluxes (mean $\text{CH}_3\text{Cl}/\text{CH}_3\text{Br}$ flux mass ratio ≈ 1600) for individual leaf litter samples (Figure 5.2b, $R = 0.75$, $P < 0.001$) suggests common processes pertaining to both gases.

Values for negative fluxes are only semi-quantitative since methyl halide uptake is limited by the initial amount of methyl halide inside the enclosure rather than by the rate of uptake by the leaf litter. Previously reported CH_3Br fluxes from leaf litter in temperate forests have been considerably higher with a mean flux of $4.3 \times 10^{-2} \text{ ng g}^{-1} \text{ h}^{-1}$ for deciduous litter and $8.0 \times 10^{-2} \text{ ng g}^{-1} \text{ h}^{-1}$ for needle litter [Drewer et al., 2008] compared to an average flux of $1.4 \times 10^{-3} \text{ ng g}^{-1} \text{ h}^{-1}$ in this study. Taking the mean and range of the flux values derived in this study and assuming a total area of $10.4 \times 10^{12} \text{ m}^2$ for tropical evergreen rainforest globally [Guenther et al., 1995] and a fine litter pool of $1537 \text{ g dry litter material per m}^2$ [Matthews, 1997] yields global annual flux values of 320 (-5.2 – 1900) Gg for CH_3Cl and 0.2 (-0.05 – 1.7) Gg for CH_3Br . This compares with the range in estimated global CH_3Cl production from tropical

Table 5.2: Mean CH_3Cl and CH_3Br fluxes for leaf litter from different parts of the rainforest. The sd values combine sampling and analytical uncertainties plus triplicate variation.

Sample plot	CH_3Cl flux ($\text{ng g}^{-1} \text{ h}^{-1}$)		CH_3Br flux ($\text{ng g}^{-1} \text{ h}^{-1}$)		% (w/w) water content
	mean	sd	mean	sd	
A	-2.4×10^{-3}	3.4×10^{-3}	-1.2×10^{-4}	1.6×10^{-4}	71
B	-5.2×10^{-3}	2.6×10^{-3}	-3.2×10^{-4}	0.7×10^{-4}	57
C	-6.0×10^{-3}	1.7×10^{-3}	-1.3×10^{-4}	0.3×10^{-4}	49
D	-3.9×10^{-3}	1.3×10^{-3}	-5.0×10^{-5}	3.1×10^{-5}	61
E	0.19	0.04	1.4×10^{-4}	0.5×10^{-4}	59
F	11	3.0	4.0×10^{-3}	1.1×10^{-3}	68
G	3.9	3.6	5.8×10^{-3}	3.5×10^{-3}	65

leaf litter of $30\text{--}2\,500\text{ Ggy}^{-1}$ derived from the Hamilton et al. [2003] laboratory study. The point estimates from this work correspond to $\sim 7\%$ and $\sim 0.1\%$, respectively, of the overall global annual fluxes of CH_3Cl and CH_3Br , respectively [Clerbaux et al., 2007]. Thus tropical leaf litter is likely to be an important source of CH_3Cl globally, but not of CH_3Br .

5.3.3 Tower profile

As can be seen in Figure 5.4 the concentration of CH_3Cl showed a marked decline with height. At 0 m height (i.e. inside the forest canopy) the concentration of CH_3Cl was almost 1000 pptV whilst at 60 m height the concentration was 740 pptV. In contrast to these findings CH_3Br concentrations (not shown) were constant throughout at 12–13 pptV and concentration differences were not large enough to draw any conclusions. Concentrations of CH_3Cl and CH_3Br were both above their global averages of 550 pptV and 7.9 pptV, respectively [Clerbaux et al., 2007]. However, these findings are in good agreement with independent measurements made on the same day at 30 m height at 13:00 by the more accurate instruments of the UEA team [Mills, 2010] who measured CH_3Br and CH_3Cl concentrations of 12.2 pptV and 1140 pptV respectively. Most remarkable is the fact that the elevated CH_3Br concentrations were only observed on this specific

day, but not on others, whereas the CH_3Cl concentrations measured in this experiment were well within the range normally observed by the UEA team throughout the last phase of the OP3 campaign. These findings strongly suggest that the forest acts as a strong net source of CH_3Cl but not of CH_3Br . It therefore fits well the observations reported in this thesis from both the branch enclosures and the leaf litter enclosures where CH_3Cl emissions were several orders of magnitude larger than CH_3Br emissions. It also adds to the suggestion that the methyl halide fluxes observed in the branch enclosures are representative for large parts of the vegetation.

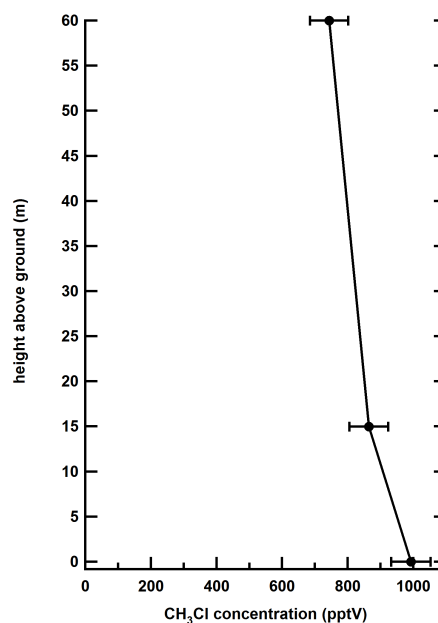


Figure 5.4: Vertical CH_3Cl concentration profile measured at GAW tower on the 10th of July 2008. Whiskers represent analytical uncertainty in concentrations.

5.4 Conclusion

In conclusion, this work confirms the few recent field measurements indicating tropical rainforests are an important global source of CH_3Cl , both via direct emissions from living plants—from species of the dipterocarp family in particular—but also via decomposing litter on the forest floor. The point estimate here of $\sim 1.4 \text{ Tgy}^{-1}$ for global tropical rainforest CH_3Cl emissions from both sources together is very consistent with the 1.3 Tgy^{-1} estimated from above-canopy concentration gradient measurements in Peninsular Malaysia [Saito et al., 2008] and the $1.5 \pm 0.6 \text{ Tgy}^{-1}$ estimated from airborne measurements in South America [Gebhardt et al., 2008].

The significance of tropical rainforests to CH_3Br budgets globally is less clear. The mass ratio of average CH_3Cl to average CH_3Br emissions from the plant species investigated here was $\sim 60:1$ which is more than double the $22:1$ mass ratio in the currently-estimated global annual fluxes of the two gases [Clerbaux et al., 2007]. This, and the much lower leaf litter CH_3Br fluxes, imply tropical forests make less contribution to global CH_3Br emissions, a few % compared with a few 10s % contribution for CH_3Cl .

However it is important to remember that raw data remain very sparse and global scale up highly simplistic. Uncertainty of emissions at the plant scale is dominated by the very large variation between species, rather than by external environmental parameters, which considerably hampers establishing quantitative connection between branch scale and above-canopy regional-scale measurements. Nevertheless it is clear that the extensive change in tropical rainforest area instigated by humankind [Sterling and Ducharne, 2008] will continue to alter global fluxes of these gases.

Chapter 6

Final conclusions

Methyl halide fluxes were successfully measured from temperate salt marshes and forests and a tropical forest site. Factors influencing flux magnitudes and flux patterns were investigated and estimates of potential global flux magnitudes were attempted. The following results were obtained:

Plants as primary methyl halide emitters

In general, methyl halide fluxes measured from living plant enclosures were considerably larger than fluxes from plant litter or bare soil, indicating that methyl halide production by higher plants could account for large parts of the missing global source of these gases (Sections 3.4.8 and 5.3.1). The main factor determining net flux magnitudes from living plant material was plant species. At Heckie's Hole salt marsh, average net CH_3Cl fluxes were positively correlated with the total dry mass of *Puccinellia maritima*, whilst average net CH_3Cl fluxes at Hollands Farm salt marsh were positively correlated to the total dry mass of *Aster tripolium*, *Juncus gerardi* and *Plantago maritima* (Section 3.4.3.1). For the tropical rain forest site this study found that species of the genus *Shorea* persistently emitted large amounts of methyl halides (Section 5.3.1). However the spectrum of tropical plants screened was not very broad and species of the family *Dipterocarpaceae* made up most of them.

From experience during the glasshouse study (Section 3.4.7) and from the law of mass action it is apparent that high amounts of bromine and chlorine in plant material favour higher production of methyl halides. However, where data were available, the differences in natural contents/concentrations of bromine and chlorine in plant material were not a direct indicator for average methyl halide net fluxes within a habitat and sometimes were even counter-intuitive (Sections 3.4.1.3 and 3.4.3.1). It is therefore arguable that natural changes in plant halogen content are probably not large enough to cause substantial flux variations.

Most importantly neither temperature nor sunlight were conclusively proven to account directly for the observed diurnal and annual flux variations of either gas from plants. However at salt marshes, temperature changes during the course of the year were found to be the best predictor of plants emissions (Section 3.4.3.2). On the other hand, the correlations found were never very strong. Other possible factors such as general growth patterns or physiological changes during the different growth stages of plants are likely to be strongly dependent on temperature and/or sunlight themselves. The annual variations of fluxes observed in salt marshes are therefore likely to be directly as well as indirectly influenced by temperature and/or sunlight (Section 3.4.3.2). The measurement campaign in Borneo was not of long enough duration to evaluate this possibility and the collars in the temperate salt marshes were a mixture of many different species (Section 3.4.1.2) making it difficult to disentangle such causal relationships in detail.

More often than not there was significant correlation between the CH_3Br and CH_3Cl net fluxes from an individual collar or species (Section 3.4.3.1), or, for the case of tropical plants, higher net emissions of CH_3Cl from a species were indicative for high CH_3Br net production or vice versa (Section 5.3.1). One interesting observation was that the ratio of CH_3Cl to CH_3Br from tropical plants and salt marsh plants were very distinct. The average $\text{CH}_3\text{Cl}/\text{CH}_3\text{Br}$ mass ratio in salt marshes was ~ 2.2 (Section 3.4.8) whereas the average mass ratio at the tropical forest site was ~ 60 (Section 5.4). The only explanation that could be offered is that CH_3Br net fluxes at the tropical forest site might have been suppressed by the relative scarcity of bromine in the plant material, whilst salt marsh plants could have presented a case of saturation of plant material with both halogens. This, however, is speculative. Compared to the current estimated mass ratio of ~ 22 for the total global annual fluxes of CH_3Cl and CH_3Br , salt marshes are relatively more important for closing the source gap for CH_3Br whilst being insignificant for CH_3Cl . On the other hand tropical plants are likely to be the biggest single source of CH_3Cl , possibly accounting for up to a quarter of global emissions, but are a comparatively minor source of CH_3Br (Section 5.3.1).

The respective average CH_3Br and CH_3Cl net fluxes from the two studied salt marshes were found to be of the same order of magnitude as fluxes reported from other temperate salt marshes but considerably less than fluxes reported from Southern Californian sites (Section 3.4.8). Furthermore, CH_3Cl fluxes measured from tropical plants were of a similar magnitude to fluxes reported by Yokouchi and co-workers adding further confidence in a globally significant CH_3Cl source from tropical plants (Section 5.3.1). Currently no other CH_3Br measurement data from field studies are available for comparison with this study.

Comparison of methyl halide fluxes from litter in temperate and tropical rainforests

CH₃Br net fluxes measured from temperate deciduous and coniferous leaf/needle litter and from tropical plant litter were all of the order of magnitude of a few pgg⁻¹ dry mass h⁻¹ (Sections 4.3.2.1 to 4.3.2.3 and 5.3.2). The only other field study by Drewer et al. [2008] examining CH₃Br fluxes from temperate forest leaf/needle litter reported net fluxes which were an order of magnitude larger. Furthermore CH₃Br net fluxes reported in the former study were always positive, whereas in this study both uptake and production of CH₃Br was observed. There is currently no conclusive explanation for this discrepancy. However it should be noted that methyl halide fluxes in general were highly variable and more *in situ* measurement data are needed to constrain global budgets.

In this study the first field measurements of CH₃Cl from leaf litter are reported. Similar to CH₃Br fluxes, CH₃Cl fluxes varied by a factor of ~5 between temperate deciduous and coniferous and tropical leaf litter. Average CH₃Cl fluxes from deciduous litter were measured to be 0.98 ngg⁻¹ h⁻¹ (dry mass) (Section 4.3.2.1) compared to 0.47 ngg⁻¹ h⁻¹ from coniferous needle litter (Section 4.3.2.2) and 2.3 ngg⁻¹ h⁻¹ from tropical plant litter (Section 5.3.2).

Similar to the findings from salt marshes halogen content was not indicative of methyl halide flux magnitudes (Section 4.4) but CH₃Br and CH₃Cl fluxes were in general positively correlated with each other (Sections 4.3.2 and 5.3.2). This would indicate that both gases were produced or destroyed by the same processes. However the average CH₃Cl/CH₃Br mass ratios of emissions recorded from temperate deciduous and coniferous leaf/needle litter and tropical plant litter were ~200 (Section 4.3.2) and ~1600 (Section 5.3.2) respectively, with no apparent explanation for the difference. Although no driver of methyl halide fluxes was found it was noted that methyl halide fluxes measured for more than a year at Fir Links, a temperate forest near Edinburgh, varied significantly with season, peaking during August and September (Section 4.3.2.1). Negative fluxes were often small but, due to the measurement technique employed, could have been underestimated.

Overall it is likely that leaf/needle litter is a small source of CH₃Br globally accounting for less than 1 % of the purported global budgets whereas production of CH₃Cl from leaf litter, in particular tropical leaf litter, could account for ~10 % of global emissions (Sections 4.3.3 and 5.3.2).

Role of drivers and modelling

It has to be concluded that methyl halide fluxes are difficult to predict or to model along the line of a simplistic causal response model. Indeed almost none of the findings from previous studies could be wholeheartedly confirmed (Section 3.4.3.2). On the other hand it has been shown that it is possible to quantify methyl halide fluxes from these study objects and that measurement of seasonality (Sections 3.4.3.1 and 4.3.2.1) and diurnality (Sections 3.4.4 and 5.3.1) of fluxes from individual terrestrial ecosystems is very important. It therefore is likely that the largest gaps in the knowledge of current global sources and sinks will soon be filled with more substantial data although a reliable forecast for future scenarios based on the direct effect of changes in climate is unlikely.

Remaining uncertainties and future work

On reflection there is potential for improvement in some areas of this work. One of the main issues was that statistical testing and quality control could have been more vigorous, especially in view of the possible effects of enclosure time on plant stress and linearity of flux (Sections 3.3.2.3 and 3.4.2). Another issue was that no universally applicable factor for the spatial variations of net flux magnitudes was found. This is especially important as the great disparity between the flux measurements in Southern California by Rhew et al. [2000] and Manley et al. [2006] and the measurements in Scottish salt marshes conducted in this study remains unexplained (Section 3.4.8). To resolve this issue a measurement campaign comparing fluxes from the two study sites in Scotland to a more southern location such as Doñana National Park in Southern Spain would be most appropriate. This would enable the comparison of flux magnitudes and patterns across the two climate zones within one study, eliminating possible inconsistencies due to variations between different studies. Another possible option to address this problem would be to conduct more controlled studies in greenhouses (Sections 3.3.3.3 and 3.4.7). However, the ultimate benefit from this type of experiment is uncertain since greenhouse studies have proven more difficult than initially envisaged, especially with regards to the stability of fluxes over time.

Apart from amending already existing work there is the opportunity to study a potentially large and not yet considered source of methyl halides. New findings indicate that methane could be potentially produced in large quantities via the UV-radiation induced chemical breakdown of plant material [Vigano et al., 2008]. This reaction has hardly been studied with traditional chamber measurements since the enclosure material has to be UV-transparent. Since methyl halides are chemically very similar to methane there is a potential that a similar

mechanism exists producing these gases and possibly helps to further close the global budget gap.

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